FUMIGATION OF SNOW WITH SO$_2$ AND NO$_2$

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SUMMARY

In a series of 48 laboratory experiments, snow was exposed to SO_2 at concentrations between about 15 and 150 ppbv for times of between 6 and 12 hours. Depth profiles within the snow of the resulting unoxidized and oxidized sulfur were obtained at centimeter resolution. The ratio of the overall rate of uptake (flux) to applied SO_2 concentration yielded surface deposition velocities. The mean value obtained was 0.06 cm s^{-1}; mean values for "wet" ($\approx 0°C$) and "dry" ($\leq -2°C$) snow were 0.09 and 0.04 cm s^{-1} respectively. Uptake of SO_2 was not significantly increased by the addition of ozone at concentrations up to 300 ppb. The experimental results are compared to a physico-chemical model of uptake; the model follows the observed trends very well and gives considerable insight into the gas-phase and interfacial absorption and oxidation processes at work.

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PROPOSALS FOR FURTHER WORK

Future research is proposed to meet needs in: 1) gaining a better understanding of the effect of oxidants associated with dry deposition of SO_2 to snow, 2) assessing the importance of dry deposition of other trace gases, particularly organic acids, 3) improving our ability to determine chemical properties of snow surfaces, and 4) developing a better predictive model for gaseous deposition to snow that includes the effects of aqueous-phase transport.

1. Oxidants

In the experiments described in this report, deposited sulfur was found primarily as SO_4^{2-}. However, at times there was a delay of up to a few hours between sample melting and analysis. Deposition velocity was unaffected by ozone, contrary to theoretical predictions. Agreement between observed deposition velocities and theoretical calculations including ozone was excellent. It is thus concluded that other oxidants were present besides ozone. Their relative contributions need to be determined. There are three tasks related to oxidant research that we propose to undertake:

(a) It needs to be established that the gaseous S(IV) taken up by snow appears primarily as SO_4^{2-}. Previously fumigated snow will be separated into depth "cuts", then kept deep-frozen in sealed containers until rapid melting (e.g. by heat lamp or microwave oven) prior to analysis. Fumigation and analytical techniques will be essentially the same as for the prior work.

(b) Total and "fast" oxidant will be determined in the liquid (or

pseudo-liquid) films of the snow by a method similar to the

conductivity-change technique used for liquid-water content. One or both

of two methods will be used. A bisulfite solution at freezing point will

be added to snow, mixed well, and separated from the solid snow. The

liquid removed will be analyzed for bisulfite and sulfate as a function of

time after separation. Correction for blanks will be applied.

Alternatively, a solution of N,N-diethylene-p-phenylene diamine will be

added and the H_2O_2 content determined spectrophotometrically. Other

methods will be used to augment these, if needed. It is planned to analyze

natural snow samples over the winter and spring snow season from a variety

of locations. Snow types will range from newly fallen powder to well

metamorphosed, aged snow.

(c) The theoretical simulation of gas uptake described in this report

will be extended to include other oxidants, e.g. an even liquid-phase

distribution of hydrogen peroxide and a diffusive source of oxygen in the

(assumed) presence of metal catalysts (i.e. Fe, Mn, Cu). The relative and

total contributions of the various oxidants will be indicated by the work

already completed plus (a) and (b) above. With regard to oxygen, sampling

and analysis of selected natural snow samples for trace metals may be

needed to augment reported literature values.

2. Organic Acids

Data on the uptake of organic acids by snow appears to be practically

non-existent. One of the proposers (G.A.D.) was the first to report the

presence of formic and acetic acids in the remote troposphere; since that

time some 500 measurements of the atmospheric concentration of each acid

have been made in a variety of locations in the Southwestern U.S.A. The data are currently being prepared for publication. Concentration of each acid at Mt. Lemmon, a forested peak near Tucson, Arizona, is typically 1.3 ppb. Formic and acetic acid are the primary natural sources of acidity in rainwater (and presumably meltwater) in remote areas of the world. Latest work suggests vegetation as the dominant (direct or indirect) source.

It is proposed to determine the deposition velocities of formic and acetic acids to snowpack, using essentially the same apparatus as before for SO_2. Formic acid is highly soluble (effective Henry's law constant $\approx 10^5$ M atm^{-1}) at pH 5, so its penetration into a snowpack should be limited in the absence of drainage. Acetic acid has an effective solubility one order of magnitude less; its penetration should therefore be greater. The comparison between these two deposition velocities may be an excellent test of the theoretical model and provide insight into the liquid-film thickness in snow.

3. Snow Surface

The theoretical model shows that the ratio of air to water is the most sensitive parameter in determining the rate of SO_2 uptake by snow. Air-to-water ratio is a function of density, porosity, liquid-water content, and specific surface area. The observed sensitivity suggests that because chemical interactions in the liquid-water film on snow grains depend on the amount of (bulk-phase) liquid, monitoring those reactions would be a way of determining relative film thickness.

A determination of the _chemical_ pseudo-liquid film thickness is crucial for both the theoretical model and for understanding gas-snowpack

interactions. Previous investigations of water in thin films have focused on determining a _physical_ film thickness; because of solvent-solute-surface interactions, the effective thickness for chemical reaction may be quite different. A totally independent determination of this important parameter is thus highly desirable. The approach will involve a few careful experiments together with additional theoretical modeling.

Initially, snow will be thoroughly purged with nitrogen before fumigation with SO_2 and ozone in excess nitrogen. Assuming that the $H_2 O_2$ contribution is small (as has been suggested by the work to date), comparison between measurement and theory will then indicate liquid-water thickness. Subsequently, a study will be made of the feasibility of using two other gases (one of which is moderately soluble), whose aqueous species react, in order to determine the film thickness by comparison with theoretical work.

4. Drainage

Drainage of meltwater needs to be included in the theoretical model of gas deposition and reaction given in this report. Melting and drainage provide new surfaces of higher pH liquid water near the snowpack surface and therefore increase deposition velocities, This interaction needs to be quantitated and clarified, looking at both gas-snowpack interactions and also the expected composition of the resulting meltwater. Flux of meltwater in the snow will be simulated using existing models. A set of experiments involving meltwater transport and collection during snow fumigation is also proposed. Initially, isothermal conditions below the snowpack surface are proposed to simplify the physical model and enable focusing on chemical changes.

INTRODUCTION

General

The dry deposition of SO_2 and NO_2 to snowpack is an area of surprisingly little previous work, (Whelpdale and Shaw, 1974; Barrie and Walmsley, 1978; Dovland and Eliasson, 1976; Granat and Johansson, 1983; Cadle et al., 1985). Most studies to date have instead emphasized the wet and dry deposition of particles, (e.g. McMahon and Denison, 1979; Slinn, 1977; Scott, 1981; Garland, 1978) and a few, (e.g. Brimblecombe and Dawson, 1984; Summers, 1977) have been concerned with precipitation-borne transport of gases. In neither the particulate nor the precipitation case is the nature of the snow surface significant in determining deposition.

Dry deposition of gases, by contrast, involves physical and chemical interactions between the gas and the snowpack; the extent of interaction will vary, perhaps drastically, depending on the nature of the snow, e.g. wet or dry, metamorphosed or freshly fallen. Existing data give little information on the interaction of the principal acid gases and snow, and none on how this interaction varies with snow type.

The acidity of snowpack is a subject of considerable concern. During melting, ion concentrations in snow decrease, and concentrations in early meltwater are up to 2-5 times those in the original snowpack. This acid shock is well documented (e.g. Haapala et al., 1975; Johannessen and Henriksen, 1978; Skartveit, 1981; Skartveit and Gjessing, 1979), and its importance well recognized. It is surprising that the contribution of gaseous dry deposition to this acidity has been so little studied. Particularly disturbing is the absence of physical and chemical models to simulate the interaction with snowpack of the most likely acid gases, i.e.

HNO_3 , NO_2 , organic acids and SO_2 , with or without oxidants. The research described here was proposed to help rectify some of these deficiencies.

Objectives

The purpose of the current study was to elucidate the physical and chemical interactions affecting the uptake of SO_2 and NO_2 by snow. The uncontrollable variabilities and changes inherent in field work were to be minimized by placing homogeneous samples of snow in a laboratory reactor and exposing them to controlled conditions of gas concentration, temperature, melting, illumination, etc. Specifically, it was proposed to investigate experimentally:

(a) whether the concept of surface deposition velocity (v_d) is valid for SO_2 and NO_2 ,

(b) what the range of values of v_d is,

(c) what is the effect of other components, particularly the ubiquitous ozone, on deposition velocity, and

(d) whether v_d is affected by illumination, temperature, and exposure time.

Theoretical

The results of the experimental work (above) are, by their nature, limited in applicability. Rather than attempt to duplicate experimentally all possible conditions under which uptake of SO_2 by snow might be important, it was clearly of the utmost urgency to develop a theoretical model to describe this uptake. The model could then be fine-tuned against the results obtained in the experimental phase, and used to predict uptake under a wider range of conditions.

BACKGROUND

The rate at which a surface exposed to the open atmosphere takes up some particular gas depends on two main factors; (a) the rate at which the gas can be transported to the surface, and (b) the rate at which the gas is absorbed by and into the surface, once there. Figure 1 (a) shows the traditional deposition model. Flux of gas from the reference level to the absorbing interface (taken as a surface) must be constant with z:

$$F = (D+K) \frac{dC}{dz} \tag{1}$$

where D and K are molecular and eddy diffusion coefficients respectively, and C denotes concentration. Between z_r and z_o the resistance to gas transfer is determined primarily by eddy transport, and therefore depends on atmospheric stability. This resistance is termed the aerodynamic resistance, r_a. Between z_o and the plane of final gas absorption there is a diffusional resistance and a true surface reaction resistance, the relative contributions of which cannot usually be separated. We shall term this combined resistance the surface resistance, r_s. The impermeable lower boundary has no effect in this model. The total transfer resistance r is therefore:

$$r = r_a + r_s \tag{2}$$

and the overall deposition velocity, v_d, its inverse:

$$v_d = 1/r = (r_a + r_s)^{-1} \tag{3}$$

Deposition velocity, flux, and concentration at the reference level are related, by definition:

$$v_d = \frac{F}{C(z_r)} \tag{4}$$

Rather than modeling the gas sink in the snow as a surface, it would be more appropriate to consider it as a diffuse sink; the snow is a
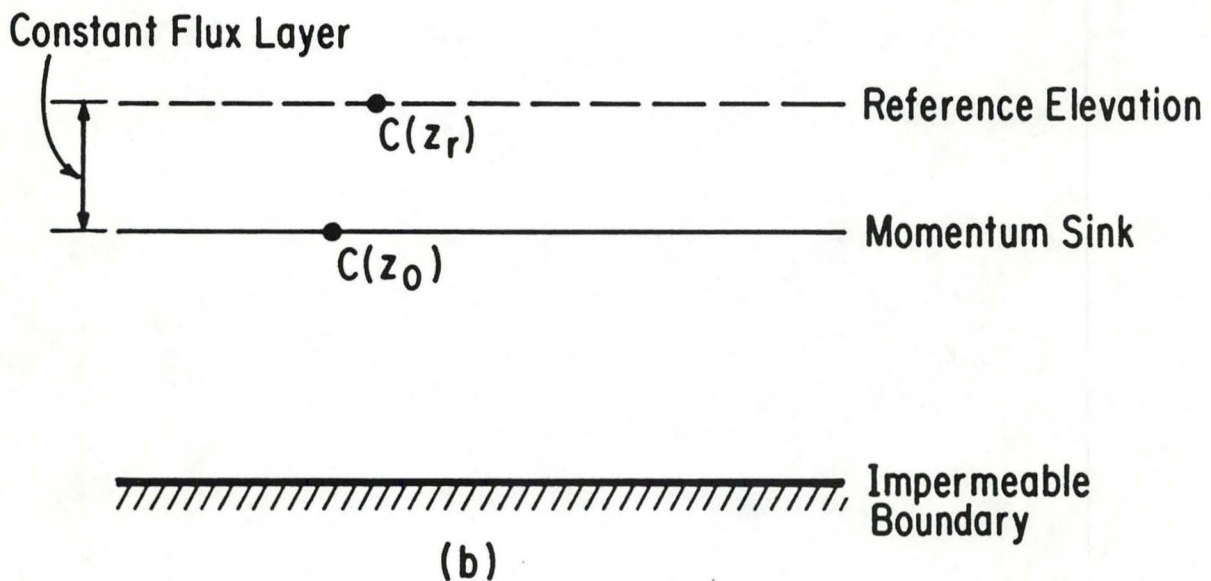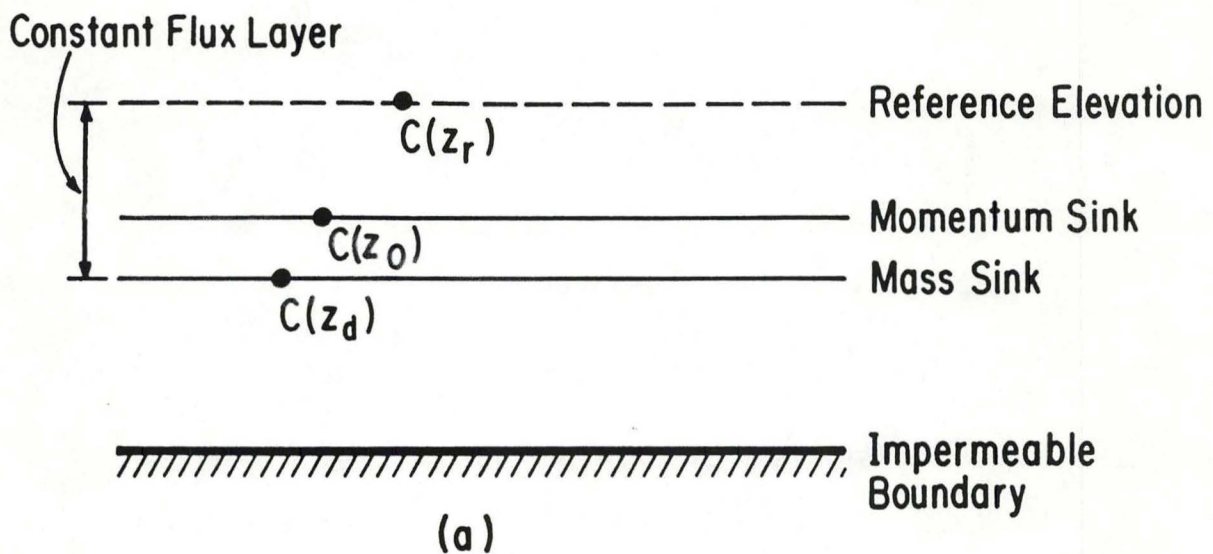
Figure 1. Conceptual Model of Gaseous Deposition:

a) Traditional model for deposition through constant-flux layer to mass sink below snow surface (momentum sink).

b) Physically based model for deposition through constant-flux layer into porous media, with flux decreasing with depth; mass may reach impermeable boundary, depending on reactivity within porous media.

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porous medium extending down to the impermeable boundary (ground), as shown in Fig. 1(b). In shallow snow, this lower boundary could have a major effect on uptake. Within the porous snow, the distinction between the planes of absorption and molecular diffusion become lost; the constant flux layer extends from reference level to the snow surface. Beneath the surface, the flux decreases with depth.

For deposition to a porous medium, three cases that involve fundamentally different mathematical formulations should be considered:

1. The atmosphere above the surface is well mixed such that $C(z_r) \approx C(z_o)$, and r_a can be neglected; a porous diffusion, reaction, etc. model can be used to describe r_s and therefore r.

2. The atmosphere above the snowpack is <u>not</u> well mixed, but can be described by a constant flux; for large concentration gradients, equation (1) provides an adequate description of the resistance; a physically-based model for surface resistance is not needed.

3. The atmosphere above the surface is <u>not</u> well mixed, but the concentration gradient is small due to a large surface resistance; a porous diffusion, reaction, etc. model can be used to describe r_s, but the small difference between $C(z_r)$ and $C(z_o)$ should be accounted for by equation (1).

To see how these cases apply to field and laboratory experiments, one needs to first evaluate typical aerodynamic resistances to be encountered in the atmosphere. This is most easily done from results on a gas that is very readily taken up by the absorbing surface, e.g. highly soluble HNO_3 or NH_3 to a wet surface. For this situation, in the field, virtually all transfer resistance will be aerodynamic (case 2 above). Previously

measured deposition velocities of HNO_3 vapor to moist surfaces range from 0.24 cm s^{-1} for stable night hours (Pierson et al., 1986) to nearly 5 cm s^{-1} for unstable daytime conditions (Huebert, 1983; Huebert and Robert, 1985). These give a spread, then, of aerodynamic resistances to be encountered in field work of about 4 to 0.2 cm^{-1} s

These resistances can be compared to the surface resistance to be expected for SO_2 on snow. It will be seen below that surface deposition velocities of SO_2 to snow are on the order of 0.05 cm s^{-1}, i.e. there is a surface resistance of about 20 cm^{-1} s. This is five to forty times the typical range of atmosphere aerodynamic resistances. In a field experiment, most of the concentration gradient will appear in the diffuse absorbing medium (case 3 above); a diffusion/reaction model can then be used to describe the interaction. In this case, vertical concentration gradients in the air are a poor way of determining gaseous deposition velocities; by far the best method uses an exposure chamber, as here.

In the laboratory, and specifically in the experiments described below, the snow surface was exposed to a stream of SO_2-laden air. The mixing provided by the gas flow ensured that concentration gradients above the snow were negligible (case 1 above). Again in this case, a diffusion/reaction model can be used to describe the gas interaction that results in the observed surface resistance r_s. The similarity of cases 1 and 3 for SO_2 on snow shows how data obtained in a laboratory study (case 1) can be applied to the field (case 3).

Using snow fumigation techniques, uptake is determined either by depletion of SO_2 in the gas supply, or, as here, by analysis of the snow. This latter method also allows vertical profiles within the snow to be obtained, considerably elucidating the uptake mechanisms.

PREVIOUS WORK

Whelpdale and Shaw, (1974) measured differences in SO_2 concentration at 2 and 8 m above snow. They compared the gradient with that above water, which was assumed to be an almost perfect collector. The gradient above snow was one third of that above water and there was considerable scatter. Deposition velocities over the snow were derived from micrometeorological theory and gave $0.05 - 1.6$ cm s^{-1} for stable and unstable conditions respectively.

Barrie and Walmsley (1978) made one determination of deposition velocity (0.25 cm s^{-1}) and calculated 40 others from a climatological dispersion model. They obtained geometric mean deposition velocity of $0.3 - 0.4$ cm s^{-1}.

Dovland and Eliasson (1976) measured sulfate accumulated in snow and SO_4^{2-} and SO_2 in the air 2 m above the surface. A deposition velocity for SO_2 of 0.1 cm s^{-1} was inferred under stable conditions and low wind speed.

Granat and Johannessen (1983) put snow into a chamber and passed air containing SO_2, NO_2, or NO through it. From the difference in concentrations of input and outlet air, an uptake was determined and a corresponding deposition velocity calculated. Granat and Johannson found negligible uptake of NO_2 or NO, and an uptake of SO_2 that would correspond to a deposition velocity of ≤ 0.1 cm s^{-1}.

From a field study in northern Michigan, Cadle et al. (1985) reported an average deposition velocity of 0.15 cm s^{-1} for snow with an appreciable exposure time above $-3°C$, and 0.06 cm s^{-1} for samples that remained below $-3°C$.

METHODS

General

This study was undertaken near Flagstaff, Arizona at the U.S. Forest Service Fort Valley Research Station, elevation 7400 ft. Experiments were conducted over a four month period, December, 1985 through March, 1986. Overall, the weather during the study period was mild and precluded the accumulation of a deep snowpack at the research station. Night time temperatures were generally -3 to -7°C, and day time temperatures were nearly always above 0°C. Experiments conducted in January were performed on the available snow, which was from an early winter storm in late November. This snow was very well metamorphosed, with rounded snow grains of 0.5 to 1 mm diameter. During February of the study period there were several snow storms, which allowed experiments to be conducted on new snow with densities of 0.09 to 0.20 g cm^{-3}. Between storms, however, temperatures during the sunny days rose to highs of 5 to 12°C, rapidly melting much of the new snow. There were also a few snowstorms in March, between which the temperatures were mild, melting much of the snowpack. Snow samples were collected from a snowpack that ranged in depth from 75 cm in early January to 40 cm in mid March.

Laboratory Studies

Snow was exposed to SO_2 within a reaction chamber made from a four-liter Pyrex beaker; the lip had been removed and the edge thickened and ground flat. Inlet and outlet tubes were attached near the top. A fused quartz window set into a teflon lid sealed the top of beaker and allowed in ultraviolet light (95 percent transmittance down to 210 nm). A snow lifter consisting of a plexiglass plate attached to two stainless-steel rods fitted inside the reaction beaker. The snow lifter permitted snow to be

removed from the beaker without disrupting or contaminating it. This
reaction chamber was placed in an insulated ice chest, dimensions 40 cm x
40 cm x 80 cm, lined with copper tubing. At one end of the chest a
"radiator" heat exchanger and fan were installed. Coolant was pumped from
an external, temperature-controlled refrigeration unit through the tubing
and radiator. A window made of two separated sheets of 1/16-inch
ultraviolet transmitting plexiglass (95 percent transmittance down to 240 nm)
was set into the top of the chest above the reaction vessel to allow
sunlight to reach the snow surface. A schematic diagram of the reaction
chamber is shown in Figure 2.

Air was pumped over the snow surface at a rate of 3 liters per minute.
The air was drawn from a large inlet immersed in outside snow. This served
to remove particles and gases that might interact with the snow sample
under study, and to achieve temperature and humidity equilibration. The
air was then pumped by a stainless-steel bellows pump through a cooling
coil immersed in snow, a glass-wool particle filter, a copper
temperature-equilibration chamber within the chest, and finally the reaction
vessel. The outlet air was analyzed for ozone. In later runs, the air
passed through an eight-foot-long coil of copper tubing within the chest to
ensure full temperature equilibrium. SO_2 , O_3 , or NO_2 were added to the air
stream just before it entered the reaction chamber.

Two different SO_2 sources were used during the experiments. The first
SO_2 source consisted of a bubbler containing a buffered solution of sodium
bisulfite. The bubbler sat in a bath of ice-water to maintain a constant
temperature for the solution. Nitrogen bled through the bubbler slowly
stripped the solution of SO_2 and carried it into the ice chest where mixing

SO$_2$ Source

Quartz Window

Inlet

Snow Sample

Reaction Chamber

O$_3$ Generator

Stainless-Steel
Bellows Air Pump

Air Inlet

Cooling Coil
and Filter
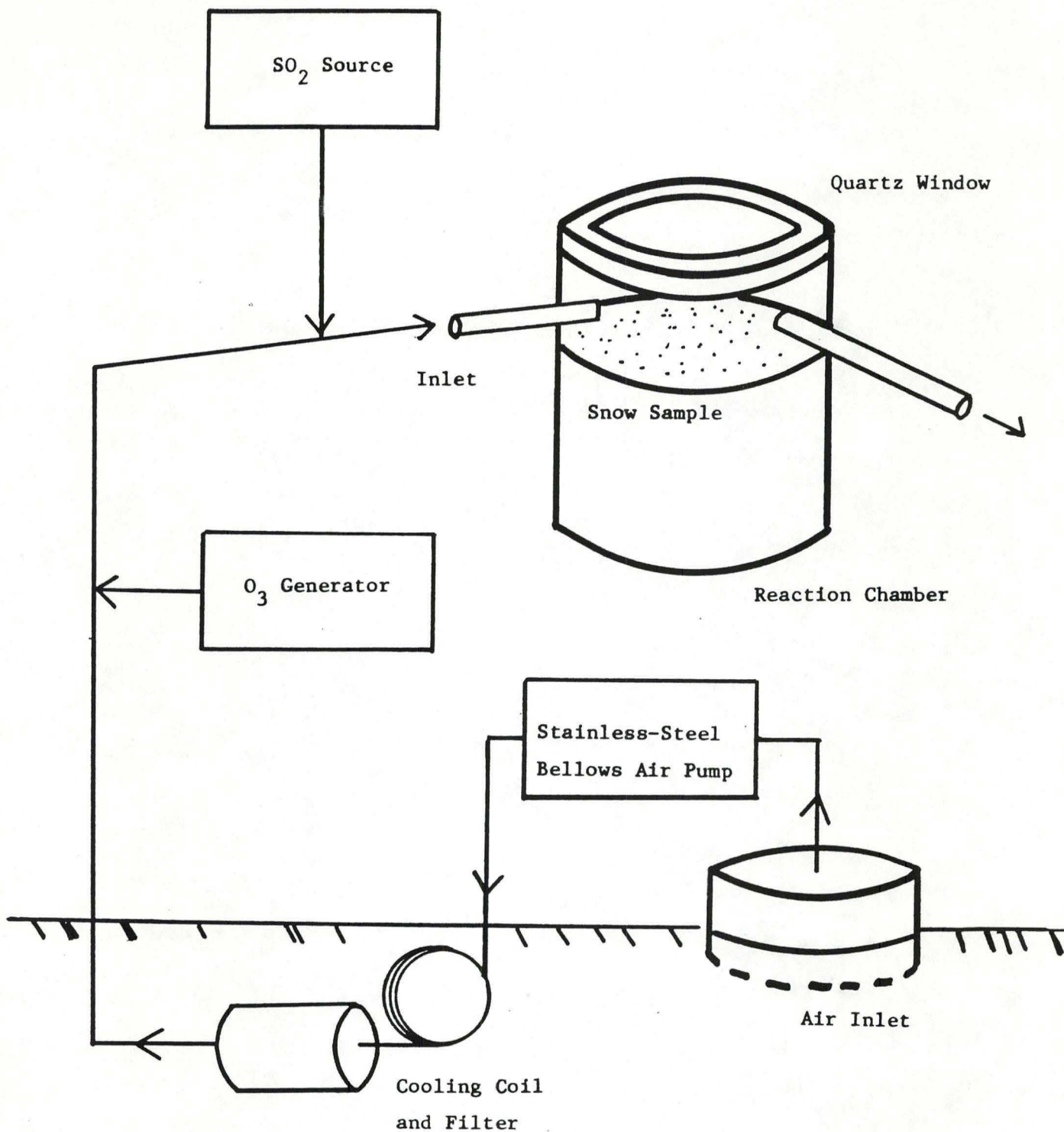
Figure 2. Schematic Diagram of Experimental Apparatus.

with the main air flow occurred. Later work used a pressurized tank of SO_2 in nitrogen.

The SO_2 concentration of the total airstream was not measured; rather the concentration in the source flow was determined and the overall concentration calculated from dilution. The SO_2 was absorbed in a liquid scrubber containing 15 mL of 10^{-3} N NaOH and a few drops of 3 percent H_2O_2. The gas flow was 2 to 12 mL min^{-1}. After absorption, the solution was heated to destroy excess H_2O_2, before analysis on the ion chromograph.

The source of ozone was an ultraviolet ozone generator fed by compressed air; concentrations were measured with a Dasibi 1003-AH analyzer. NO_2 in nitrogen was supplied by Matheson Gas Co.; no means were available to check the NO_2 concentration.

The snow-handling procedure was as follows. The snow lifter was placed in the reaction beaker, and the whole apparatus was cooled to the desired operating temperature. Snow, generally below 0°C was collected from 5-15 cm below the snowpack surface with a trowel, broken up, and sifted through a 3x4.5 mm mesh screen to remove clumps. The homogenized snow was then poured into the beaker and the lid was secured. Air, to which the SO_2 and sometimes ozone was added, was passed over the snow for 6 to 12 hours. At the end of an experiment, the lid was removed and a plexiglass snow sampler (Fig. 3) inserted into the snow down to the plate at the bottom. The snow and the sampler were then removed together using the lifter. Snow in the sampler was divided into one- or two-centimeter cuts and the separated samples transfered into containers. The melted sample was ana- lyzed for bisulfite, sulfate, nitrate, and chloride using a Dionex ion chromatograph; pH was determined with Radiometer combination electrode and Altex pH meter.

Handle

Sliding Front
Panel

}1cm

Divider

3.3 cm

Bevelled Edge
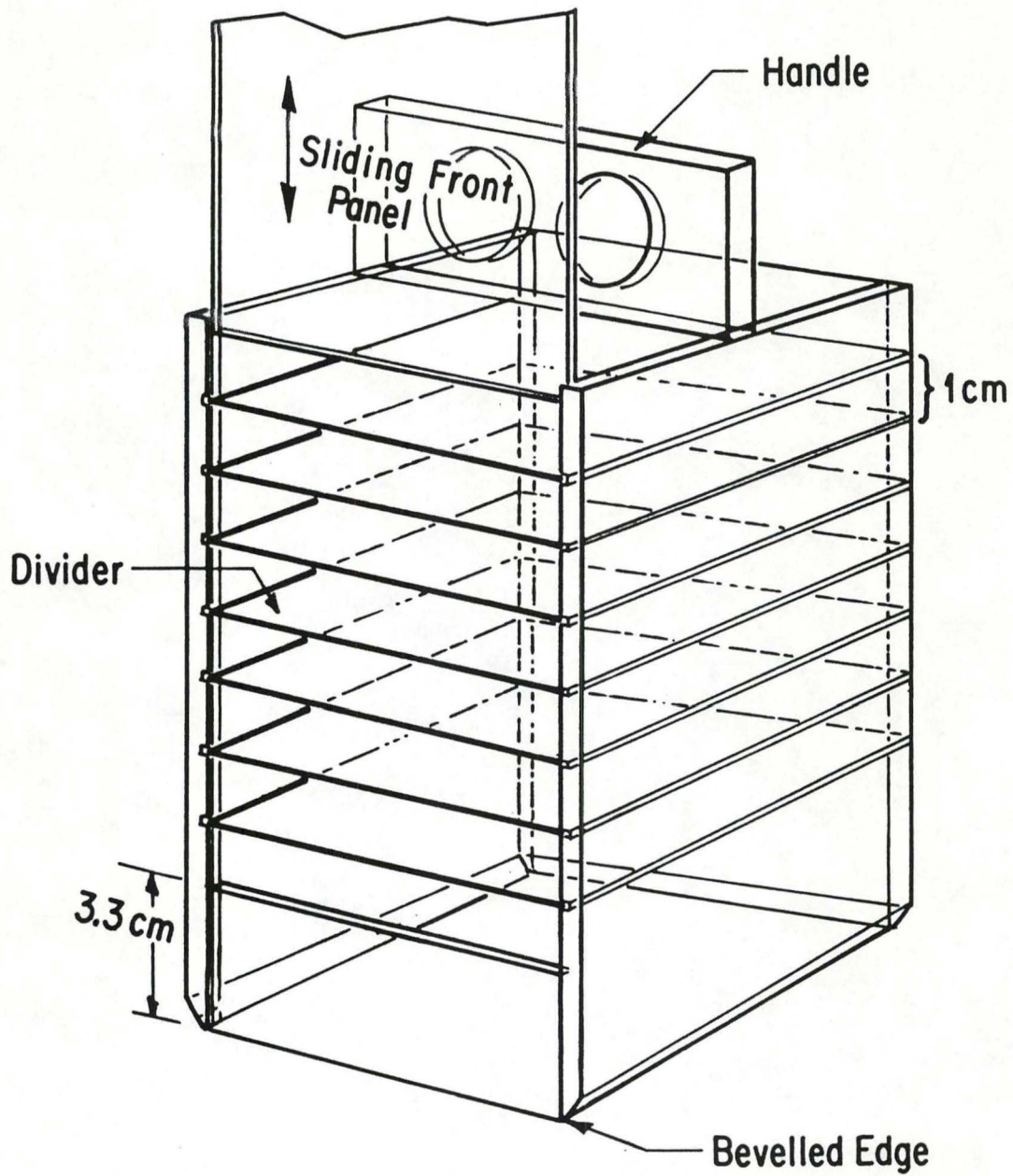
Cross-section Area: 94 cm^2 (9.7cm x 9.7cm)

Figure 3. Snow Sampler (not quite to scale: the snow sampler was taller and had more dividers).

Temperature within the ice chest was measured with a thermistor placed beside the reaction chamber and a mercury-in-glass thermometer above it. In the absence of sunlight the two temperatures were the same. In sunlight, the thermometer indicated the snow-surface temperature; the thermistor was in the shade and represented the temperature deeper within the snow. Thermistor temperatures are given in Table A-1.

In-Situ Studies

Several fumigation experiments with SO_2 were conducted either on the undisturbed snowpack or on snow which had been piled up into a mound if the natural snowpack was too shallow. The experimental arrangement is shown in Figure 4. Air, to which SO_2 and ozone were added, was pumped by a stainless-steel bellows pump to the inside of the stainless-steel ring above the snow. Flow rate was 9.5 L min^{-1}. In some experiments, the upper open part of the ring was covered with an ultraviolet-transmitting plate of plexiglass to reduce the effects of wind loss of gas, while allowing in sunlight. Exposure times were typically 6 hours. Prior to fumigation, density samples were taken, and blank samples were collected to establish background snow characteristics. After fumigation, snow was collected with the sampler as in the laboratory studies, separated into depth "cuts" and analyzed.

In general, the in-situ work was unsatisfactory. There were unexplained losses of SO_2, presumably to the stainless steel ring, and perturbations due to wind losses that could not be eliminated. As a result, the concentrations of SO_2 in the air above the snow were poorly known and the experimenters had little confidence in the data derived. No results of in-situ measurements of deposition velocity will be presented in this report.
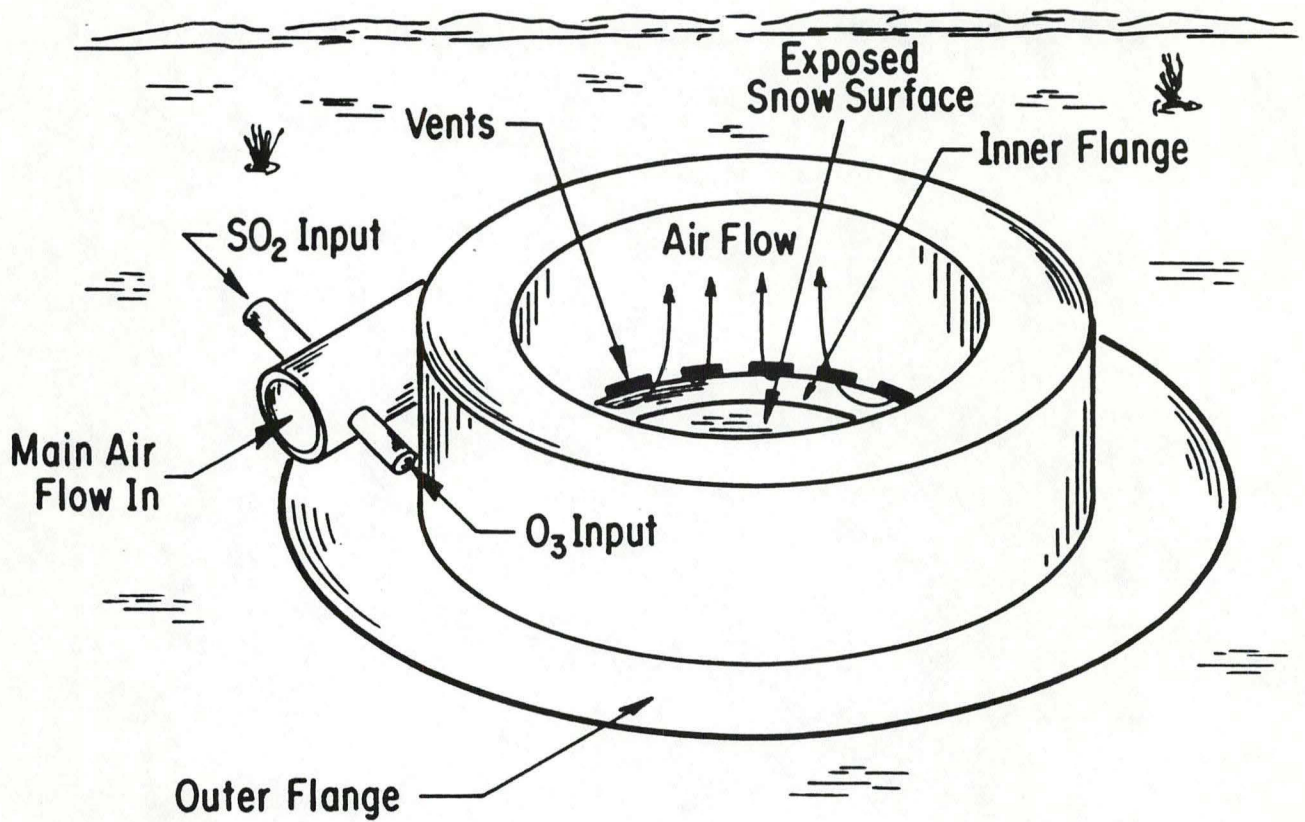
Figure 4. In Situ Apparatus.

Physical Properties of the Snow

Liquid water content. The procedure used to determine the liquid water content (LWC) of the fumigated snow essentially followed the methods of Davis et al. (1985) and Perla and LaChapelle (1984). Some minor modifications were made as a result of conditions at Fort Valley and available equipment. A calibration curve was developed to test the accuracy of the technique prior to use on snow samples.

As detailed in Davis et al, (1985) the determination of liquid water content is based on measuring the change in conductivity of a dilute acid stock after it is added to, mixed with, and extracted from a snow sample of known mass. Decreases in the conductivity reflect the amount (mass) of liquid water. More specifically, the mass fraction of liquid water (X_w) is calculated from:

$$X_W = \frac{W}{M} = \frac{S}{M} \frac{(1-C_m)}{(C_m/C_s)-(C_w/C_s)} \tag{5}$$

where W is the unknown mass of water, M is the wet snow sample mass, S the stock solution mass, C_s the concentration of impurity ions in the liquid water and C_m the concentration in the extracted liquid. Concentrations are determined from the conductivity measurements by the nonlinear relationship $C_m/C_s = (G_m/G_s)^\alpha$ where G_m is the specific conductance of the extracted mixture and G_s is the conductance of the stock solution. The α exponent, determined experimentally from a series of acid-water dilution tests of conductivity changes, was 1.0461. The acid stock solution was diluted to approximately 0.007 M HCl, which had a measured specific conductance of ~ 1800 μ Scm^{-1} at 23°C. The conductivity of snowmelt was less than 2.0 μ Scm^{-1}, so that the ratio of C_w/C_s was negligible. All conductivities were measured at 23°C.

A calibration curve was developed from 61 trial runs using known amounts of water and snow. The absolute error of the trial runs was 1.7 percent, comparable to the calibration error of Davis et al. (1985) of 1.2 percent, and Perla and LaChappelle (1984) of 1.7 percent.

Density. Density of the snow collected for fumigation was determined gravimetrically. Measured weights of three samples obtained in cylinders of known volume (100 cm^3) were averaged for a given run. Measured density reflected snow age and degree of metamorphism. Snow falling at temperatures near 0°C had densities ranging from 0.15 to 0.22 g cm^{-3}. Densities of snow falling at colder temperatures (<-2.0°C) were around 0.08 to 0.10 g cm^{-3}. Snow which had fallen two months prior to the experiments was well metamorphosed, with grain size of ~2 mm, well rounded, and with densities of 0.36 to 0.45 g cm^{-3} (average 0.4 g cm^{-3}). During warm days (+5 to +10°C), which often followed a snowfall during the study period, snow density rapidly increased as metamorphism and melting/sublimation occurred.

Air permeability. Air permeability was measured using two different permeometers, both of which were to be used with Darcy's equation:

$$Q = (K)(A) \, \Delta P/L \qquad (6)$$

where Q is the flow rate of air (cm^3 s^{-1}), L is the lengh of snow sample (cm), A is its cross-sectional area (cm^2), ΔP is the pressure difference (cm of water) and K is the air permeability (cm^2 s^{-1} cm^{-1} H_2O. Air permeability depends on the properties of both the fluid and the porous medium. Intrinsic permeability, k, depends only on the medium:

$$k = K\mu / \gamma$$

where μ is the viscosity of air (1.7×10^{-4} g cm^{-1} sec^{-1} at 0°C) and γ is the specific weight of air ($\approx$ 980 gm cm^{-2} sec^{-2} at 0°C).

In the first permeometer, pressure difference was maintained constant

and air flow was measured (in situ method); in the second, air flow rate was held constant and pressure difference measured (pipe or cylinder method).

Problems were encountered with both devices. The greatest uncertainty was introduced by the inclined manometer used for pressure measurements, which exhibited a lack of reproducibility. In addition, the cylinder permeometer presented problems of even loading of the snow into the cylinder. The snow, especially low density snow, would often clump, resulting in cracks and cavities. Table 1 compares the air permeability values determined in this project with three other studies. The K values reported for the Fort Valley new, fine-grained snow are from measurements made after the snow was tapped slightly to settle it.

The in situ method using constant pressure drop typically gave air permeabilities a factor of two lower than by the cylinder method.

Analytical Methods

Snow concentrations of anions SO_4^{2-}, NO_3^-, HSO_3^- and Cl^- were determined using a Dionex ion chromatograph and appropriate standards. The cations sodium, calcium, and magnesium, in a few selected samples of old snow, falling snow, and a core from nearby Mt. Humphreys were determined by atomic absorption spectrophotometry. The pH of all samples were taken at the time that the sample was melted.

Table 2 shows typical background chemical composition for snow samples at Fort Valley during the sampling period. Falling snow samples showed higher levels of SO_4^{2-} and NO_3^-, when collected towards the beginning of the storm. During one long storm of February 8, falling snow was collected at the beginning (am) and the end (pm) of the storm. Anion

Table 1. Air Permeability and Density Comparisons

Source, snow type	Air Permeability $cm^2 \ s^{-1}$ (cm H_2O^{-1})		Intrinsic Permeability cm^2 (average)	Density, kg/m^3	
	range	average		range	average
This study					
new, fine grained	75–1990	1900	3.3×10^{-4}	80–220	90
fine-grained, compacted	35–450	370	6.4×10^{-5}	220–330	190
coarse	60–3400	230	4.0×10^{-5}	350–650	410
Martinelli (1971)					
new	10–40	—	—	70–300	—
fine-grain, old	5–50	—	—	250–470	—
coarse-grain, old	30–200	—	—	300–500	—
Conway & Abramson (1984)					
new	200–490	—	—	70–150	—
fine-grain, compact	20–250	—	—	100–490	—
coarse grain	140–300	—	—	400–550	—
Shimizu (1970)					
new	500–1250	—	—	50–130	—
fine-grain, compact	50–300	—	—	120–460	—
coarse-grain	75–300	—	—	350–550	—

Table 2. Representative Values for Chemical Composition of Snow at
          Fort Valley, 1986 (concentration in ppb).

Snow Type	pH	$SO_4^=$	NO_3^-	Cl^-	Na^+	Ca^{++}	Mg^{++}
Spring Snow 1 Week Old (February 27)	5.36	108	264	110	30	25	50
Well Metamorphosed (8-sample average March 3-19)	5.48	60	190	100	125	20	10
New Falling Snow (March 12)	5.26	140	290	106	64	<10	<10
1-3 Day Old Snow (7 day average, February 5-12)	4.94	360	920	170	--	--	--

concentrations show a large decrease and pH a significant increase from morning to afternoon. Old snow, which had fallen one month before the study period, exhibited lower concentrations of SO_4^{2-} and NO_3^-. This probably is the result of the snow having undergone some melting, which tends to concentrate the impurities in the meltwater. Measured pH values of new and falling snow were also lower (≈ 4.8) than for older, well metamorphosed snow (≈ 5.3). Ion balances on melted snow typically showed anions (SO_4^{2-}, NO_3^-, Cl^-), greater than cations (Na^+, Ca^{2+}, Mg^{2+}, H^+).

RESULTS

Summary

Results are summarized below, as related to the four objectives listed in the Introduction. Table A-1 (Appendix) is a summary of all 48 experiments.

(a) The concept of deposition velocity is applicable to SO_2 on snow, but only as a first approximation. The question is complicated by the need (in any experimental study) to expose a snow surface to higher-than-ambient levels of the gas, thus changing the snow surface, i.e. the pH. Further details on this complex question are presented in the Discussion section below.

Figure 5 shows a plot of 47 of the 48 SO_2 fluxes measured in this study as a function of SO_2 concentration (one value fell off scale). The line labeled "3" is the best fit passing through the origin to the complete data set and has a slope of 0.058 cm s^{-1} for mean surface deposition velocity.

Figure 6 shows 47 of the 48 SO_2 deposition velocities obtained, plotted as a function of SO_2 concentration. Even neglecting the few very high values (which could have resulted in
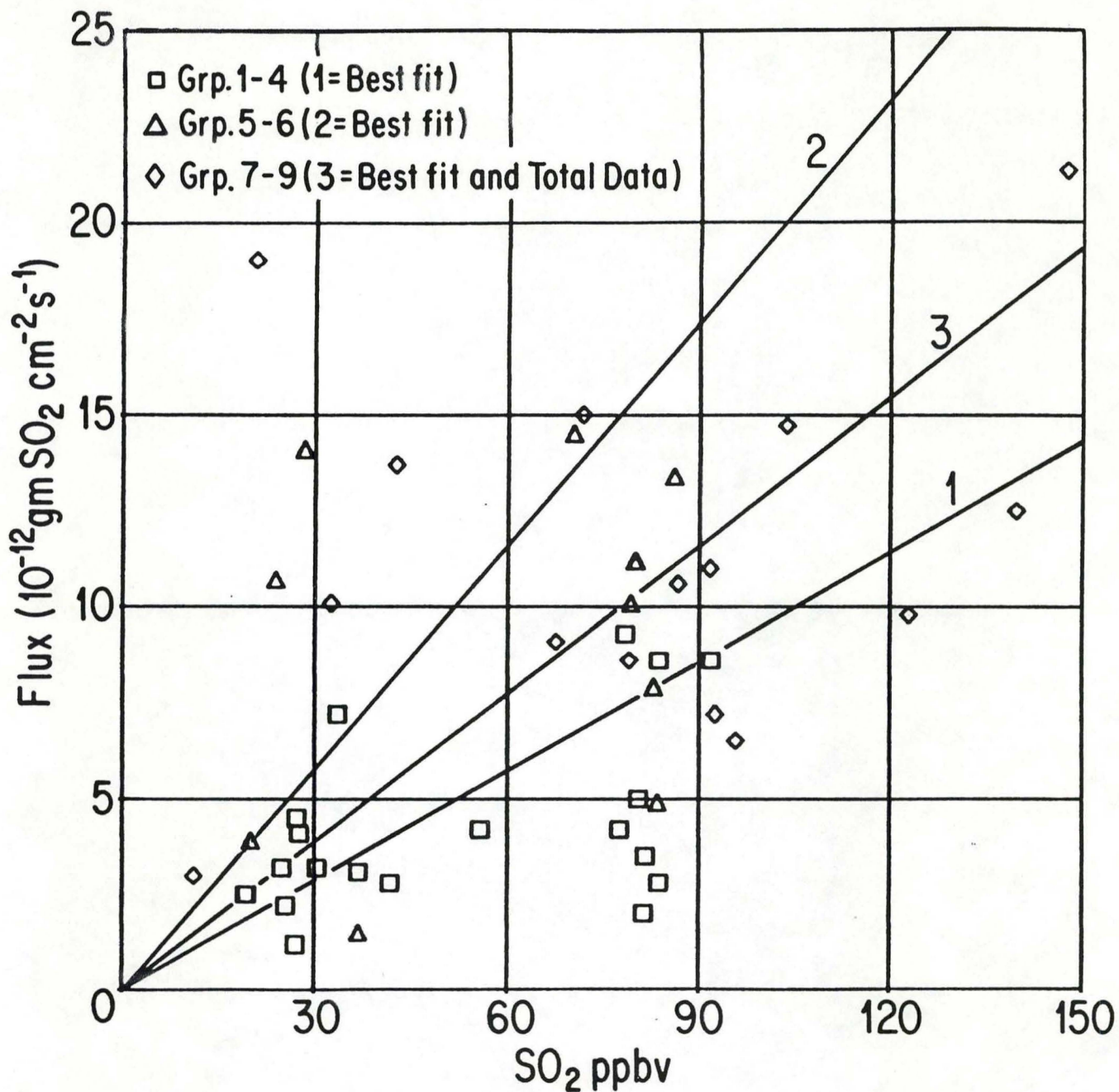
Figure 5. SO₂ Flux vs. Concentration:

Line 1: Best fit for Groups 1-4 (no sunlight, low temperatures).

Line 2: Best fit for Groups 5-6 (no sunlight, temperatures near 0°C, little or no draining).

Line 3: Best fit for Groups 7-9 (with sunlight), and best fit for total data.
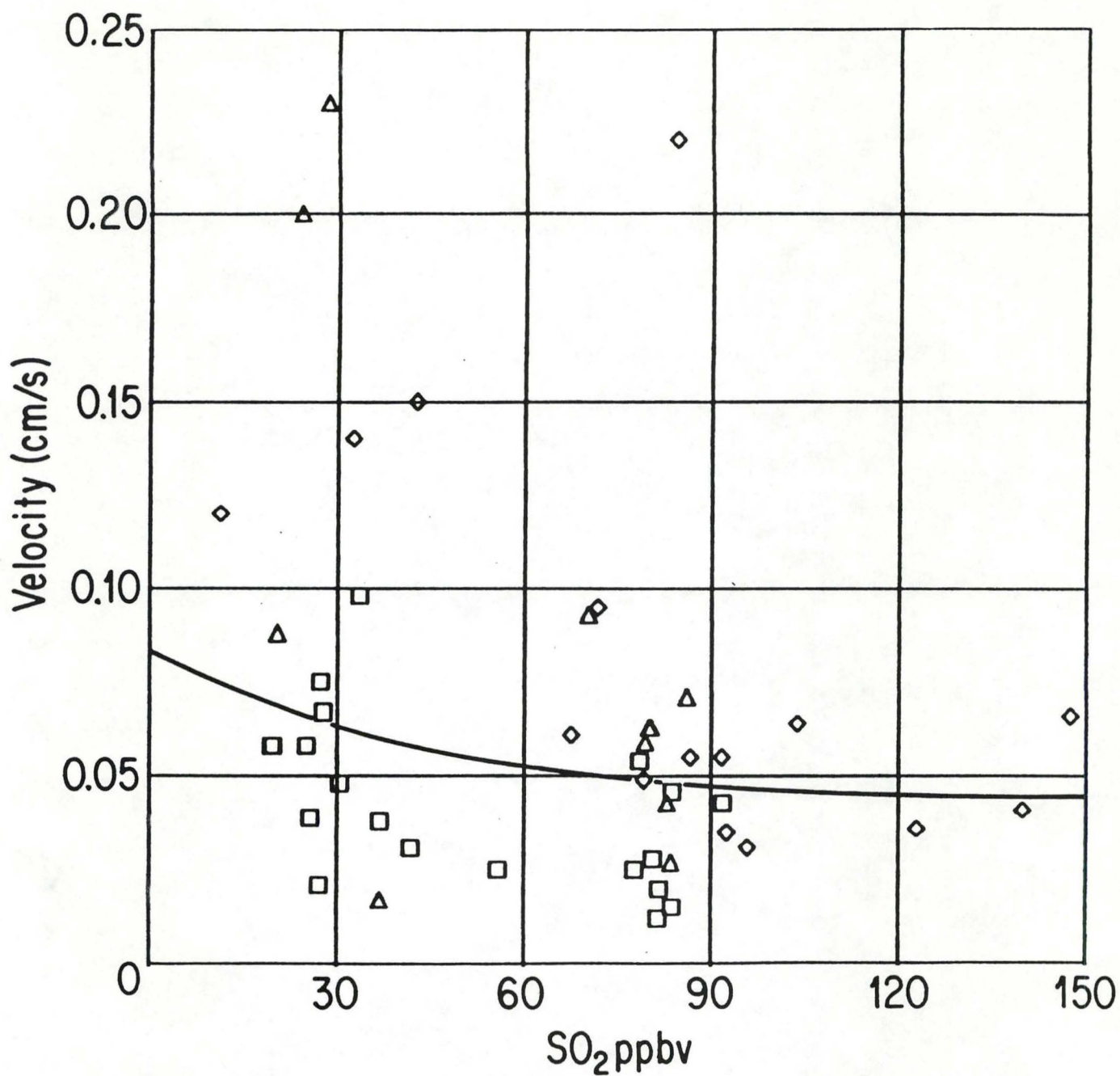
Figure 6.   SO$_2$ Deposition Velocity vs. Concentration (curve drawn by eye).

part from non-representative blanks), a tendency for the velocity
to decrease slightly with increasing concentration is suggested
by the curve drawn (by eye) through the points.

(b) The lower line in Figure 5 represents the best fit for snow of
varying texture and density but experiencing no melting; the
slope is 0.043 cm s^{-1}. The upper line gives the best fit for all
snow undergoing some melting but little draining; the slope is
0.087 cm s^{-1}. All of these values are from laboratory
investigations.

(c) The surface deposition velocity of SO_2 was negligibly affected by
the addition of ozone. Figure 7 shows deposition velocities for
all conditions of texture, density, illumination, temperature,
etc. as a function of ozone concentration. No trend is
distinguishable. Comparison between individual experiments gives
the same result. In view of our prior laboratory experience this
was initially surprising, though a theoretical model (see below)
is consistent with a relatively small ozone effect on deposition
velocity _per se_.

(d) In the absence of melting, the surface deposition velocity of
SO_2 was found to be negligibly affected by sunlight that had
passed through fused quartz and ultra-violet-transmitting
plexiglass.

The range of temperature studied was not large (-9°C to
0°C), and over this range, in the absence of significant melting,
no clear temperature dependence of deposition velocity was
observed. The influence of melting has been noted above.

The deposition velocity did seem to be slightly affected by
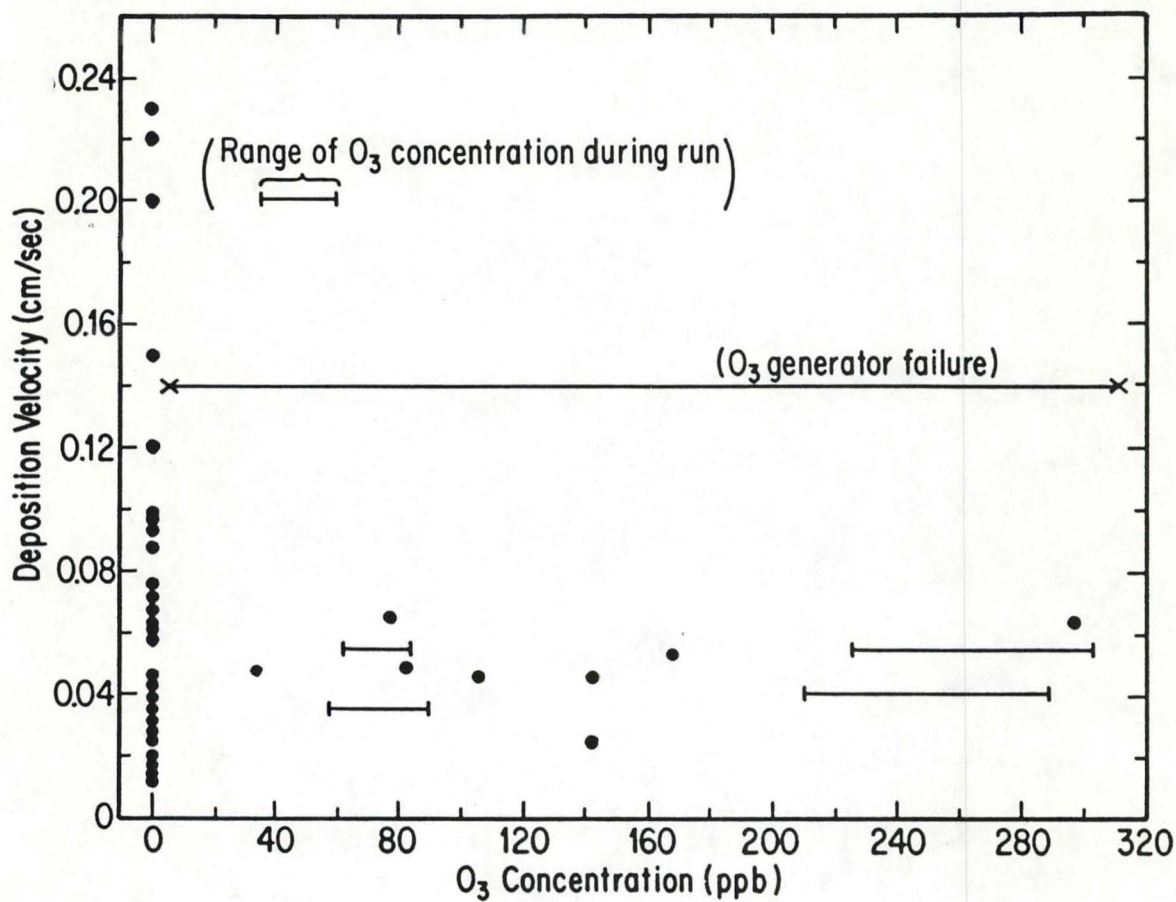
Figure 7. SO₂ Deposition Velocity vs. Ozone Concentration.

exposure time and history. The laboratory results were
suggestive but not totally conclusive; the theoretical treatment
(see below) predicts a decrease in surface deposition velocity
with exposure time.

Profiles

The profiles obtained in each of the 48 sulfur dioxide runs of this
study are shown in Figures A-1 through A-8 (Appendix). Experiments can be
divided into three main categories on the basis of temperature and
illumination. Subgroups further distinguish experiments on the basis of
snow age, liquid water content and ozone exposure. In the profiles,
sulfate concentrations are shown by the white bar, bisulfite by the black bar.

In the first major category, temperatures were sufficiently low ($<-1°C$)
to prevent melting of snow; surfaces were not exposed to sunlight. Twenty-
one of the experiments fall into this category; they are divided into four
groups:

1. Low density, new snow at temperatures ranging from -1.9 to -2.4C;
   no sunlight and no ozone added. Profiles are shown in Figure A-1.
   Penetration of sulfur down to at least the 7 cm depth was observed
   in most experiments, with only one (2-16A) exhibiting a steep
   concentration profile. Most uptake was found as S(VI), despite the
   absence of ozone. SO_2 concentration was 20-30 ppbv, except for
   2-16A, where it was 90 ppbv, and 2-08A, where it was about 35 ppbv.
   Two experiments were on freshly-fallen snow (2-04A & 2-06A); snow
   in the others was 1-2 days old. The four experiments under the
   most constant conditions (2-05A, 2-09A, 2-10A, and 2-11A) exhibit
   good reproducibility, both qualitatively (profiles) and

quantitatively (deposition velocities 0.03- 0.06 cm/s). For all
eight experiments, deposition velocities were in the range
0.03-0.07 cm/s. At the lower SO_2 concentrations, no S(IV) is
present, but it is present at the higher concentrations.

2. Medium-density, new snow at -2°C, with no sunlight, but with 140
ppbv ozone added; SO_2 was 75-80 ppbv. Profiles (Figure A-2) are
steeper than in the experiments with lower SO_2 and no ozone given
above, and resemble the other high-SO_2 experiment (2-16A); a
significant difference is the virtual absence of S(IV) in the
experiments with ozone present. Deposition velocities are in the
range 0.02-0.05 cm/s, i.e. somewhat lower than in group 1. However,
the snow in group 1 had a higher specific surface area.

3. Older snow, no sunlight and no ozone; temperatures were -2 to -2.3°C
and SO_2 was 80 ppbv. Profiles are given in Figure A-3. Uptake was
small (deposition velocities 0.01-0.03 cm/s, with the higher value
from the six-hour experiments (2-21A & 2-26A); other experiments
were for 12 hours. However, the snow in 2-21A and 2-26A was only
6 and 11 days old, respectively, versus several weeks in the other
three. The lower uptake of these high-density, aged snow samples
may have been the result of air/snow surface area differences. The
greater relative amount of S(IV) present is consistent with the
higher SO_2 and the absence of ozone. Conditions were very similar
in the five experiments of this group; the results illustrate the
reproducibility of the experimental method.

4. Other low temperature experiments on old snow. Profiles are given
in Figure A-4. Uptake and deposition velocity for run 1-08A are
little different from those in group 3, although the temperature

was much lower. The other four experiments were preliminary

measurements whose results are generally consistent with other low

temperature data. Numbers 1-04B and 1-05B were conducted at night;

the ozone added failed to give the S(IV)→S(VI) conversion noted in

later work (group 2). Both experiments started with wet snow that

re-froze during the experiment. Number 1-06A had similar crusting

problems.

In the second category, temperatures were near zero, some melting

occurred, but experiments were not exposed to sunlight. Eleven of the

experiments fall into this category.

5. Experiments at or near 0°C, no ozone, and little or no draining, old

   snow. Profiles are given in Figure A-5. Two distinguishing features

   of these profiles, as compared to those with colder snow (e.g. group

   3) are the much greater uptake in the upper snow layers and the

   greater fraction of the total uptake present as S(IV). Dissolution

   of SO_2 in the liquid water in the upper layers results in the

   concentration-depth profiles being much steeper. Deposition

   velocities are 0.02-0.09 cm s^{-1}. The low uptake below the surface

   layer (and, hence, the low overall deposition velocity) in

   1-09B was not observed in other experiments; one difference in

   conditions was that 1-09B was run at night when intake (outside) air

   was colder (-2 to -8 C) than during the day, when it was above 0°C.

   Among the remainder of the runs, the highest deposition velocity

   (0.2 cms^{-1} for 2-02A) is observed at the lowest SO_2 concentration.

   Errors in blank or background adjustment cannot be excluded.

6. Experiments at or near 0°C, no ozone, and no draining; medium-density new snow: 2-03A, 2-17A. The two profiles in Figure A-6 differ from the previous nine (group 5) in that little S(IV) remains in the profile. Deposition velocities are somewhat higher: 0.23 and 0.07 cm/s; this may be due in part to the less dense snow. The starting temperature for 2-03A was +3°C in the reactor, which could partially be responsible for the higher uptake.

The last category consists of 16 experiments, carried out in sunlight. They are presented in three groups in order of increasing sunlight intensity, temperature and draining:

7. Older snow, with surface melting, but without significant draining of meltwater, due to the maintenance of cold (< -3.5°C) temperatures. Profiles are given in Figure A-7. Number 1-14A was exposed to lower intensities of sunlight; 1-21A was run on a colder day. As a result, in both cases, temperatures were correspondingly lower and melting less. Number 1-21A shows lower uptake despite the addition of ozone. SO_2 concentrations in 1-14A varied somewhat, making it less suitable for comparison. Nevertheless, neither profile contained unoxidized sulfur. With increasing melting in the other experiments, steeper concentration gradients and more bisulfite were seen, associated with the liquid water at the top of the snow. Most had ozone added; one exception being 2-12A, which has a slightly less steep concentration profile. Experiment 2-12A also had a very low SO_2 concentration (11 ppbv), and a high deposition velocity (0.12 cm/s). For the others, deposition velocities were 0.04-0.07 cm/s.

8. Medium-density snow, with significant draining due to surface melting, but cold (< 2°C) reactor temperatures. Profiles are shown in Figure A-8. Draining occurred primarily along the snow-lifter rods. Deposition velocities (0.03-0.09) were little different from those for comparable experiments without draining (group 7). A large fraction of the SO_2 deposited ended up in the bottom of the sample, however. Experiment 3-20A has no S(IV) present; this may be the result of the applied ozone, and some delay in completing the analysis.

9. Old snow, with intense sunlight, with significant draining due to the surface melting, and near 0°C reactor temperatures. Profiles are given in Figure A-9. Deposition velocities for these four experiments were high (0.14-0.41 cm/s) due to the large amount of draining. The highest value (for 1-11A) was for the lowest SO_2 concentration, consistent with group 5 results. S(IV) is highest in 1-12A, which had no ozone present and received the most intense sunlight.

NO_2 Uptake

Four laboratory experiments on the uptake of NO_2 were completed; the results were adequate to show the essential features of the snow/NO_2 interaction. All four experiments were conducted in the presence of ≈ 120 ppb ozone. Profiles for the two experiments without illumination are shown in Fig. A-10(a) and (b); light bars show concentration of nitrate, dark bars concentration of nitrite. The influence of draining is evident in 3-18-A. In 3-17-B, without obvious draining, the profile was fairly flat

over the first eight centimeters; this is to be expected for a component having little interaction with the ice. From Fig. A-10(a) and (b), deposition velocity without illumination was only about 0.005 cm s^{-1}.

Fig. A-10(c) and (d) also show profiles from the two experiments with solar illumination. Sunlight photolyzes NO_2:

$$NO_2 \xrightarrow{h\nu} NO+O$$
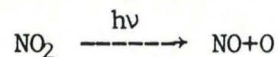
which is followed by:

$$O+O_2 \xrightarrow{M} O_3$$
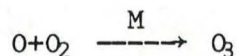
but the excess ozone speeds up the reverse reaction:

$$NO+O_3 \longrightarrow NO_2+O_2$$

so that the concentration of NO should be small. Nevertheless NO, NO_2 and water obey an equilibrium:

$$NO+NO_2+H_2O \rightleftharpoons 2HNO_2$$

and in addition

$$2NO_2+H_2O \longrightarrow HNO_3+HNO_2 .$$
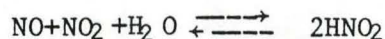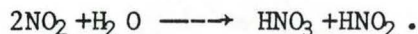
The nitrous acid is readily oxidized, or decomposes:

$$3HNO_2 \longrightarrow HNO_3+2NO+H_2O$$
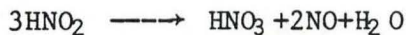
Sunlight increases the deposition velocity of NO_2 by about a factor of two, though illumination was associated with increased melting. Experiments 3-22A and 3-18A have very similar profiles, so draining should not have been responsible for the increased uptake. It is concluded that the deposition velocity of NO_2 is entirely determined by surface resistance and is small, typically 0.005 cm s^{-1}; sunlight appears to increase this by a factor of 2-2.5.

MODEL OF SO$_2$ DEPOSITION

Theoretical Model

Deposition of trace gases to snow is a multi-step process involving transport of reactants (SO$_2$, oxidants) to the snow surface, adsorption or absorption at the snow-air interface, and chemical reaction to yield products (e.g. bisulfite, sulfate). Any of these steps could limit the rate of the overall process. A simple model of this process is proposed, involving one-dimensional diffusive transport downward through the snowpack, equilibrium absorption of the diffusing species, and kinetically-limited chemical reaction in the liquid layer on the surface of snow grains. At 0°C, liquid layers on snow grains can be seen, and LWC measured. For this analysis it is assumed that a liquid layer is present on the surface of snow grains even at subzero temperatures; evidence for the existence of this layer at subfreezing temperatures has been summarized by Clifford (1975). We thus apply the concept of LWC down to values as low as 0.0001, which would correspond to a 20 nm-thick uniform liquid film on 1 mm spherical grains. One further assumption in the model is that atmospheric concentration gradients over snowpack are small, in accordance with the previous discussion on aerodynamic and surface resistances.

The chemical and physical models for deposition to wet snow are presented in Tables 3 and 4. Diffusion of SO$_2$ is retarded by absorption into the aqueous phase, given by the multiplier on the left side of equation (17). The irreversible reaction of dissolved S(IV) to form S(VI) is given by the second term on the right side of equation (17). Advective transport, surface diffusion, gas-phase reactions, etc. could be added to the model. Other chemical species are not included. At very low SO$_2$ concentrations, pH will be ~5.5 and determined by CO$_2$ equilibrium.

TABLE 3. Chemical Model for SO_2 Deposition

Equilibrium Condition

$$SO_2(g) + H_2O \overset{K_H}{\rightleftharpoons} SO_2(aq) \tag{7}$$

$$SO_2(aq) \overset{K_1}{\rightleftharpoons} HSO_3^- + H^+ \tag{8}$$

$$HSO_3^- \overset{K_2}{\rightleftharpoons} SO_3^{2-} + H^+ \tag{9}$$

$$H_2O \rightleftharpoons H^+ + OH^- \tag{10}$$

$$O_3(g) \rightleftharpoons O_3(aq) \tag{11}$$

$$H_2O_2(g) \rightleftharpoons H_2O_2(aq) \tag{12}$$

Irreversible Reactions

$$O_3 \longrightarrow \frac{3}{2}O_2 \quad , \quad \text{heterogeneous first-order rate constant} = k_{oz} \tag{13}$$

$$S(IV) \xrightarrow{\text{oxidant}} S(VI) \tag{14}$$
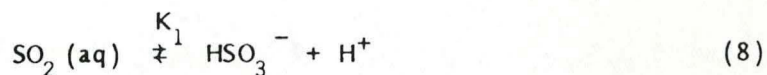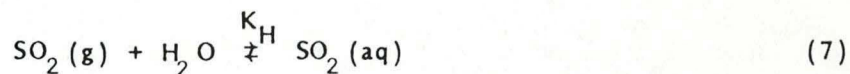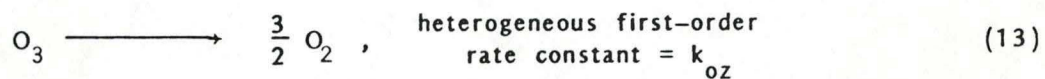
Rate Laws

$$\frac{d[S(IV)]}{dt} = -k_1[S(IV)][O_3(aq)] \tag{15}$$

$$\frac{d[S(IV)]}{dt} = -k_2[S(IV)][H_2O_2(aq)] \tag{16}$$

k_1, k_2 are experimentally determined rate constants, and are functions of pH. Square brackets denote aqueous concentrations.

TABLE 4. Transport and Reaction Model for SO_2 Deposition

Governing Equation for SO_2 (g):

Let C be the gas-phase concentration of SO_2:

$$\left(1 + \frac{K_H}{r_{aw}\alpha_0}\right)\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - \frac{k'K_H C}{\alpha_0 r_{aw}} \tag{17}$$

where

r_{aw} = air-to-water volume ratio in the snow

α_0 = fraction of aqueous S(IV) present as SO_2 (aq)

D = gaseous diffusion coefficient of SO_2

k' = pseudo first-order rate constant, $k' = k[O_3 (aq)]$

Boundary Conditions

$$C(0,t) = C_0 \tag{18}$$

$$\frac{\partial C(\infty,t)}{\partial x} = 0 \tag{19}$$

$$C(x,0) = 0 \tag{20}$$

Deposition Velocity for S(IV)

With reaction:
$$V(\bar{t}) = \frac{K_H}{\bar{t}\, C_0 \alpha_0}\int_0^x C(LWC)\,\rho_s\,dx \tag{21}$$

Without reaction:
$$V(\bar{t}) = \frac{K_H (LWC)\rho_s}{\alpha_0}\left[\frac{4D}{\pi t}\middle/\left(1 + \frac{K_H}{r_{aw}\alpha_0}\right)\right]^{1/2} \tag{22}$$

where (LWC) = liquid water content of the snow

and ρ_s = snow density

Concentration of S(VI)

$$[S(VI)] = \frac{K_H}{\alpha_0}\int_0^{\bar{t}} Ck'\,dt \tag{23}$$

Deposition Velocity for S(VI)

$$V(\bar{t}) = \frac{K_H}{\bar{t}\, C_0 \alpha_0}\int_0^x \int_0^{\bar{t}} C(LWC)\,\rho_s\,k'\,dt\,dx \tag{24}$$

Oxidants

Equation 17 includes the pseudo-first-order rate constant for the SO_2/O_3 reaction k'; k'=k[O_3 aq]. Since ozone is a poorly soluble gas, its aqueous concentration can be obtained via its Henry's law constant. Other oxidants might be present, however, e.g. oxygen (with iron and manganese catalysts), hydrogen peroxide, hydroxyl radical, etc. Given the low iron and manganese concentrations typically found in snow (Laird et al. 1986), and in the absence of pollution, it is expected that the only other significant oxidant will be hydrogen peroxide.

Hydrogen peroxide is highly soluble with a Henry's Law constant of about 6.1×10^5 M atm^{-1} at 0°C. The amount partitioned into the liquid phase will depend on the amount of liquid water available. Most outer snow crystals form high in the atmosphere in air already depleted of hydrogen peroxide. During the fall to ground, some warming occurs and a pseudo-liquid film is formed. This film will come to equilibrium with atmospheric H_2O_2. Freshly fallen snow will therefore, to a first approximation, contain a certain surface liquid water content that, if small, will be in Henry's law equilibrium with atmospheric H_2O_2, typically 0.3 ppb, (Slemr, et al., 1986), i.e. will have a H_2O_2 content of $\approx 6 \times 10^{-5}$ M. Subsequent partial melting of the snow merely dilutes this surface peroxide solution. Additional peroxide may be added to the snowpack by diffusion from the air. Because of the high Henry's law constant, its penetration will be negligible; this contribution will be neglected in the work below.

Oxidation Rate and Capacity

The rate of oxidation of SO_2 by H_2O_2 is very rapid, but the amount of oxidation is finite and very limited. By contrast the rate of reaction with

O_3 is fairly slow, but the supply of oxidant is continuous, depending only on diffusional transport from the air. Partial melting of the snow will not affect the peroxide oxidation significantly, since the reaction is fast; melting <u>will</u> increase the amount of ozone oxidation, however, since the total quantity of aqueous ozone increases correspondingly.

Aqueous-phase concentrations for S(IV) are given by modified Henry's law and for S(VI) by equation (23). Deposition velocities for the two species are given by equations (21) and (24). Deposition velocity is calculated by summing the concentrations of S(IV) and S(VI) accumulated with depth at a given time. The integration is from the snowpack surface (x=0) to some depth (x) below which concentrations drop off to small values. In the absence of S(IV) oxidation (k'=0) and for constant pH, deposition velocity is given by equation (22).

DISCUSSION

Validity of Deposition Velocity Concept

Deposition velocity is defined as the ratio of mass flux of material to its concentration at a reference level. It will change as a result of changes in either r_a or r_s. Laboratory and field data are more easily applied and extrapolated if changes in r_s are negligible over the time-scale of the experiments.

The concept of deposition velocity to snow can be applied to field situations, within certain limits. Some of the more important variables for long-term SO_2 deposition, which can cause changes in r_s are: 1) SO_2 concentration above the snowpack, 2) air-to-water volume ratio in the snowpack, 3) S(IV) to S(VI) conversion rate in the snow, and 4) aqueous-phase transport down through the snowpack.

As defined, deposition velocity should not be a function of concentration at the reference level. While it is not clear how r_a could change with concentration, variations in r_s with concentration are conceivable. The theoretical results obtained to date indicate that a porous medium (such as snow) undergoing chemical change as a result of gas uptake has a surface deposition velocity that is a function of both time and gas concentration. The importance of the latter three factors is illustrated by our experimental results, as discussed above. In addition, others have shown the importance of atmospheric conditions (r_a) on deposition velocity (e.g. Sehmel, 1980; Colbeck & Harrison, 1985)

As changes in the above factors will result in a change in r_s, longer-term deposition velocities should be valid for relatively constant conditions or regular (e.g. diurnal), repeating changes in these variables. Uptake to seasonal snow covers should relate to short-term laboratory values if longer-term field conditions can be modeled as a sum of a series of cyclical (e.g. day-night) short-term segments. One should not expect the same deposition velocity for widely-different conditions, such as mid-winter (colder, less-dense snow) versus spring (metamorphosed, draining snow) conditions, however.

Time Dependence

The change in surface deposition velocity of gas to a snow surface is indicated by the model. For unreactive gases, deposition velocity is inversely proportional to the square root of time (Eq. 22). For reactive gases, the time dependence is included in the solution for C (equation 17). For the boundary conditions given, the analytical solution involves an

error function; neither the solution nor its time derivative give a simple relation with respect to time. Deposition velocity (and C) may also be a function of the concentration of other reactants, expressed through k'.

In Figure 8 are shown computed variations with time of deposition velocity of SO_2 to snow in the presence of O_3. Conditions and assumed properties simulate those in the experiments performed here and are given in the legend. Deposition velocity decreases with time as the snow becomes more acid over a time-scale of several hours. Changes are by a factor of about two. We were unable to distinguish this change from the numerous other natural variations in the experiments.

Figure 9 shows computed variations with time of deposition velocity of SO_2 to snow in the presence of O_3 under the more realistic ambient conditions given in the legend. The change is relatively minor after the first few hours. The time-scale is certainly long enough to come into steady state with diurnal freeze/thaw/drain cycles.

The relationships shown on Figures 8 and 9 would be qualitatively similar in the presence of low concentrations of a second oxidant such as H_2O_2 or O_2 plus a metal catalyst. Slightly higher deposition velocities result, and penetration is somewhat less.

Concentration Dependence

Sulfer dioxide. As SO_2 is taken up and oxidized in the liquid or pseudo-liquid film of the upper layers of snowpack, pH decreases. This decreases the rate of oxidation by O_3 or O_2 locally and requires deeper penetration of SO_2 before much further oxidation/uptake can occur. All other factors being constant, the deposition velocity should therefore decrease with increasing SO_2 concentration in the presence of O_3 under
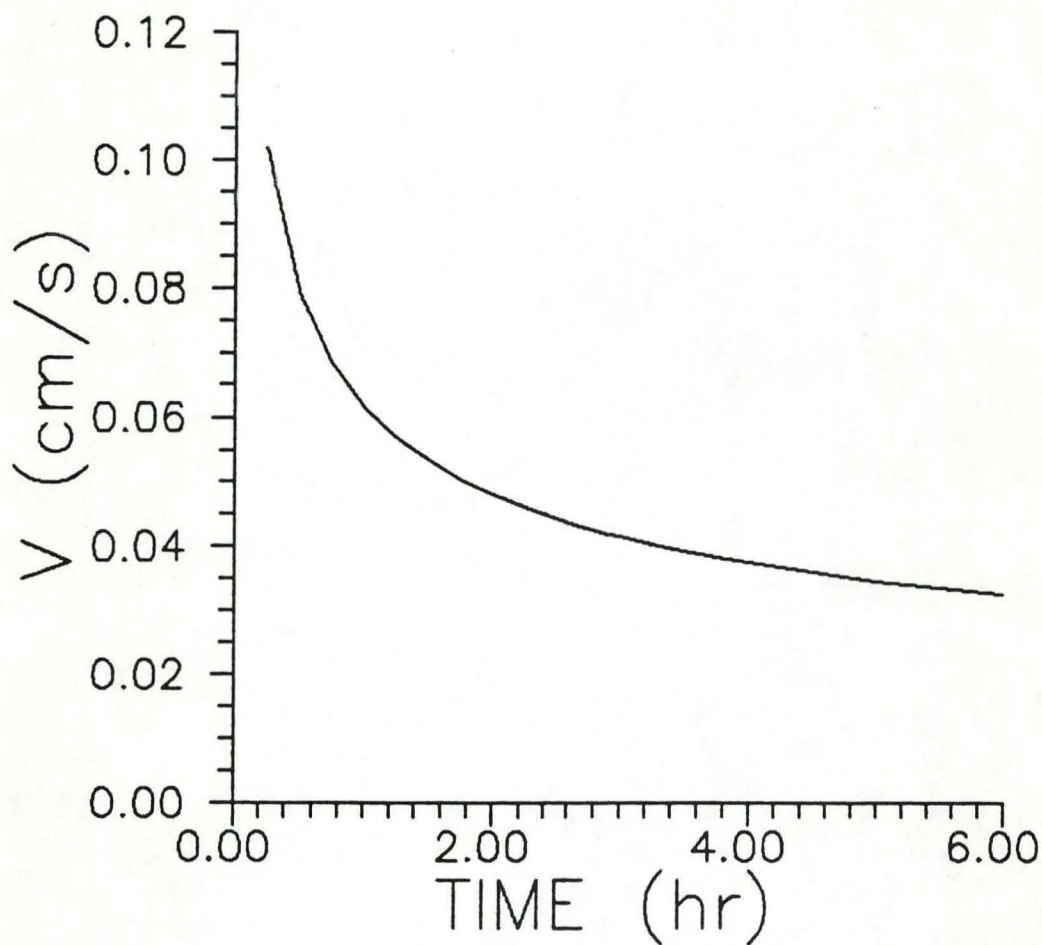
Figure 8. Calculated SO_2 Deposition Velocity vs. Time For Laboratory Conditions.
SO_2 = 20 ppbv, O_3 = 30 ppbv, LWC = 0.001, ρ = 0.4 g cm^{-3} .
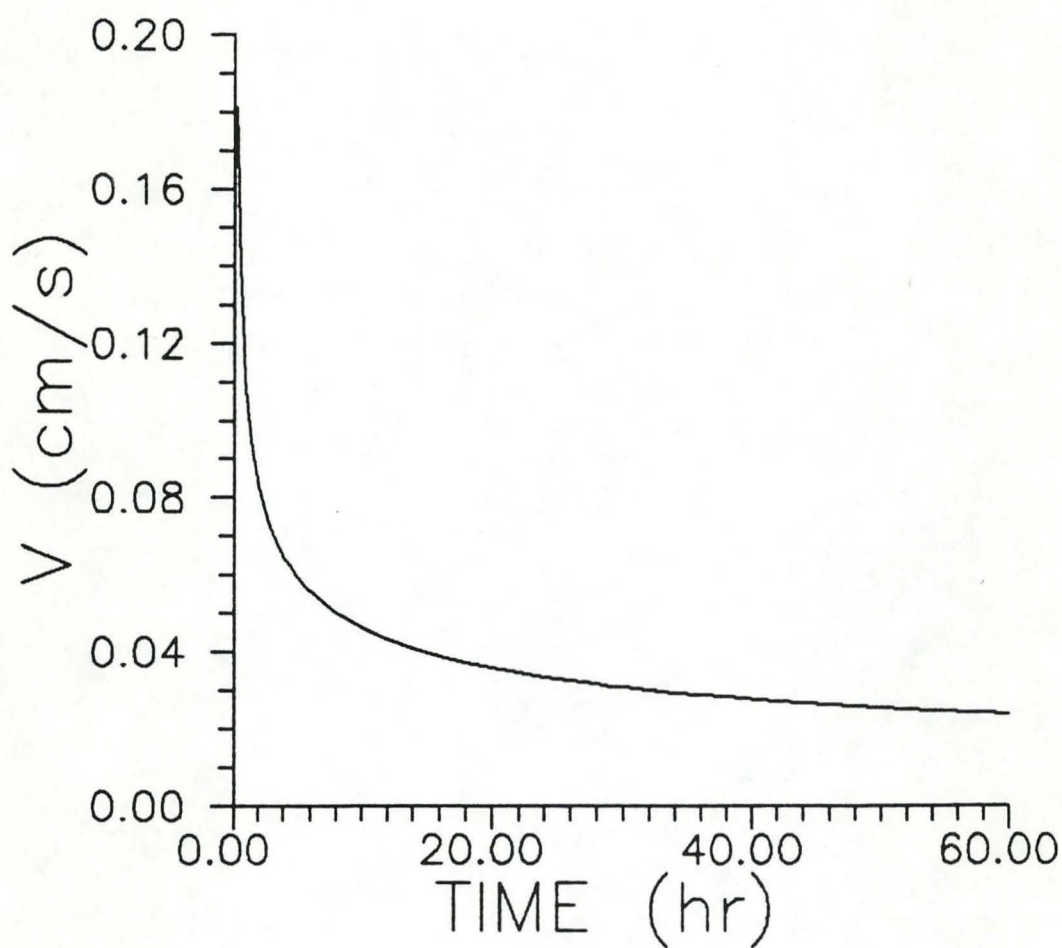
Figure 9. Calculated SO_2 Deposition Velocity vs. Time For Typical Ambient Conditions. SO_2 = 5 ppbv, O_3 = 30 ppbv, LWC = 0.001, ρ = 0.4 g cm^{-3}. Calculations done to 6 hours, with later values based on a power-law extrapolation.

conditions simulating those in the experiments above. The theoretical variation (Fig. 10) is in accord with that observed experimentally.

Ozone. Increasing ozone leads to greater oxidation/uptake of SO_2, particularly in the upper layers of the snowpack. The resulting pH decrease greatly reduces the oxidation and again requires deeper penetration of SO_2 before further oxidation can occur. Increasing ozone should therefore produce a modest increase in SO_2 deposition velocity. This effect was not distinguished in the experiments. For this reason, and the fact that much of the sulfur absorbed was found as S(VI) even at low O_3 concentrations, another oxidant should be incorporated into the snowpack model. Two possiblities are to include a uniform H_2O_2 concentration in the snow, or to include a metal-catalyzed O_2 reaction. Results shown in Figure 11 are with only O_3, under conditions simulating those in the experimental work.

Although calculated deposition velocities are similar for the different oxidants, concentration profiles change significantly. Rather smooth curves are depicted for SO_2 and pH (Figure 11a and 11b) in the presence of O_3 as the only oxidant, or with no oxidant. Adding H_2O_2 to the snow, but not the atmosphere above the snow, would give a much less steeply-sloped profile. Essentially, an "SO_2 front" diffuses downward in the snowpack; H_2O_2 is depleted above the front as SO_2 dissolves and is oxidized to SO_4^{2-}.

Effect of Liquid-Water Content

At high liquid-water contents, deposition of SO_2 is limited to the upper part of the snowpack, whereas at lower liquid-water contents
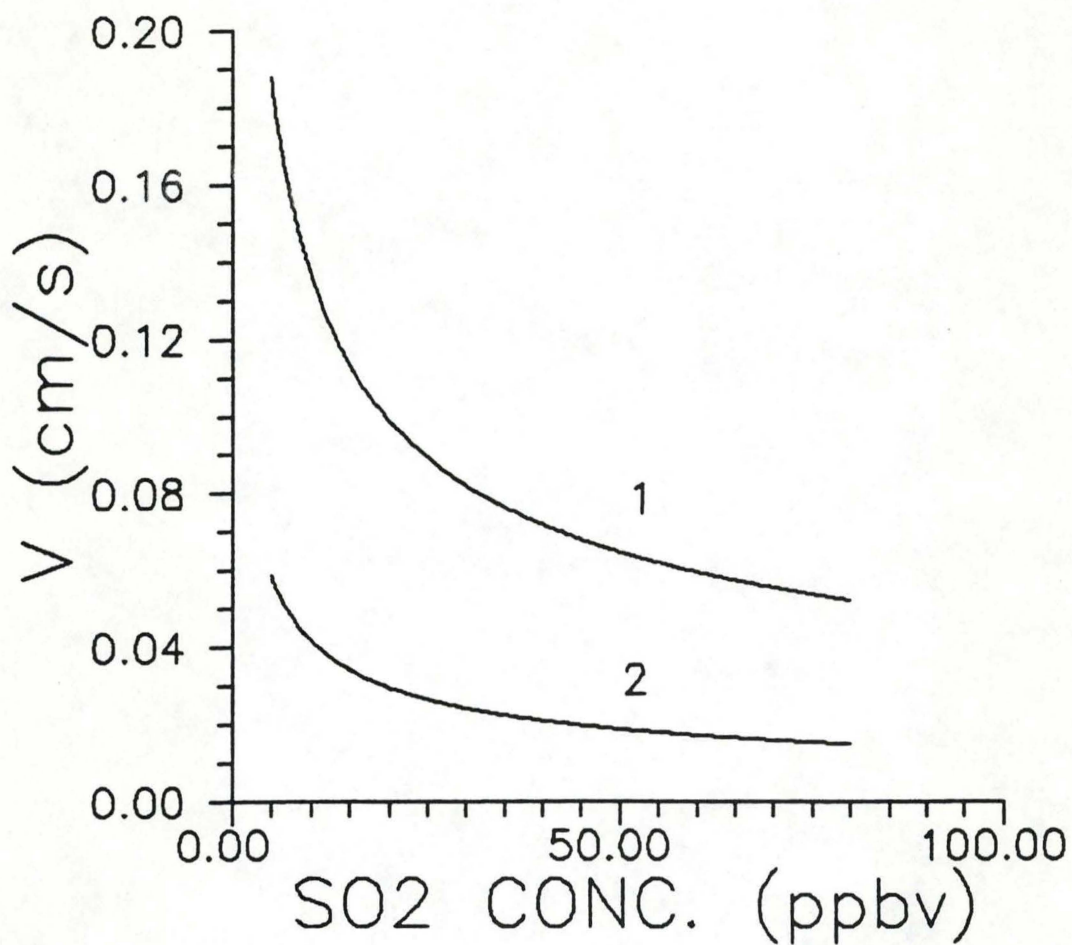
Figure 10. Calculated SO_2 Deposition Velocity vs. SO_2 Concentration. O_3 = 30 ppbv, ρ = 0.4 g cm^3, T = 6 hr.

Line 1:   LWC = 0.01
Line 2:   LWC = 0.001
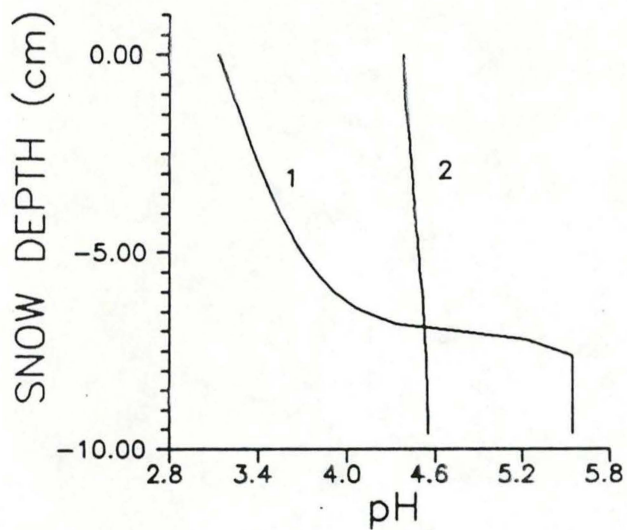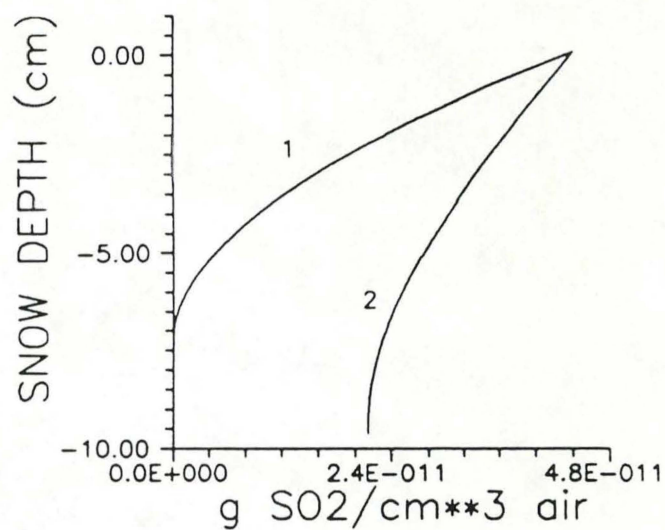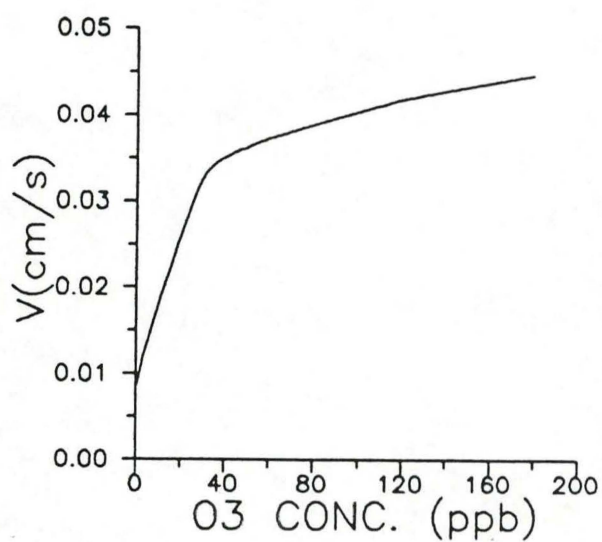
Figure 11. Calculated SO_2 and pH Profiles, and SO_2 Deposition Velocity vs. Ozone Concentration. SO_2 = 20 ppbv, ρ = 0.4 g cm^{-3}, LWC = 0.001, T = 6 hr.

Figs. 11a and 11b — Line 1: O_3 = 30 ppbv

Line 2: O_3 = 0 ppbv

penetration is much greater. This is illustrated experimentally by comparing our results for 0°C versus below 0°C (i.e. Figures A-5 vs. A-1). Snow from several experiments conducted at 0°C were analyzed for liquid water. There was no clear relationship between measured LWC and deposition velocity, although the presence of meltwater and drainage did affect the distribution of the sulfur taken up.

Figure 12a shows the same effect for model calculations at different liquid water contents but constant oxidant concentration. The effect of LWC after 6 h on v_d is illustrated on Figure 12b. Deposition velocity decreases by a factor of 4 for a 10-fold decrease in LWC (10-fold increase in air-to-water ratio).

Effect of Temperature

In the absence of changes in liquid-water content, changes in deposition velocity over the temperature range encountered in seasonal snowcovers should be small. The temperature effects noted previously in field measurements of SO_2 deposition (Cadle et al., 1985) should be due primarily to changes in liquid water content. The model results for deposition velocity, penetration depth, etc., are particularly sensitive to this parameter.

Effect of Snow Physical Properties

Deposition velocity should depend on the specific surface area of snow at temperatures below 0°C. Assuming that below-freezing snow or ice has a liquid or pseudo-liquid layer with a thickness that is independent of surface area, more SO_2 should be absorbed in snow with a larger specific
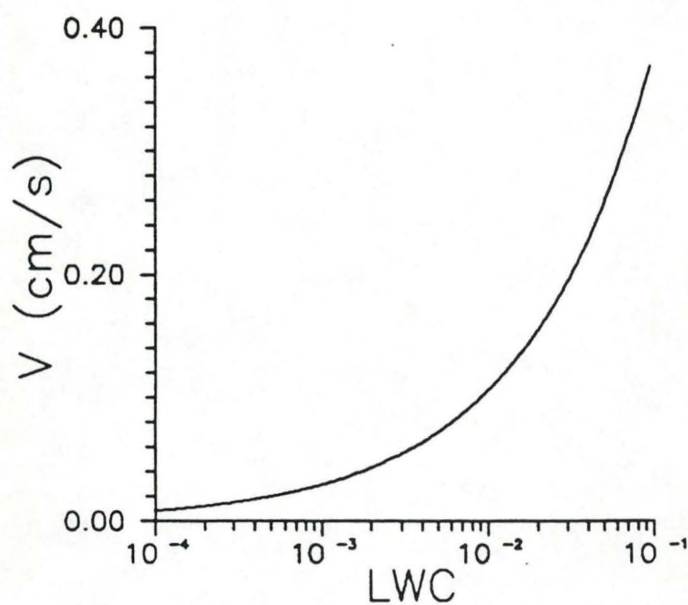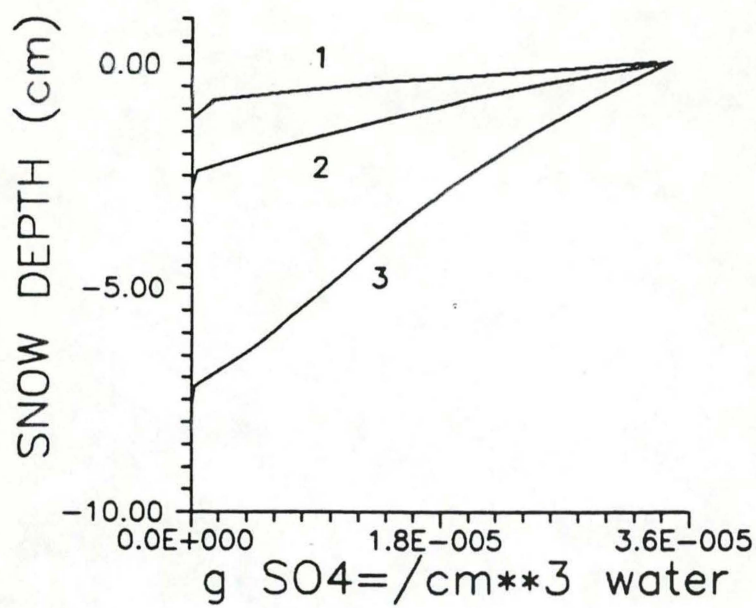
Figure 12. Calculated $SO_4^=$ Profile and SO_2 Deposition Velocity vs. LWC. $SO_2 = $ 20 ppbv, $O_3 = $ 30 ppbv, $\rho = 0.4$ g cm^{-3}, T = 6 hr.

Fig. 12a – Line 1: LWC = 0.1
Line 2: LWC = 0.01
Line 3: LWC = 0.001

surface area. Qualitatively, this trend was observed in going from old snow to new snow (Figures A-3 to A-1). New snow had a higher air permeability and lower bulk density than old snow. However, no quantitative correlation could be established between specific surface area, calculated from empirical relations with density and air permeability, and deposition velocity.

CONCLUSIONS

Laboratory snow samples have been exposed to SO_2 and NO_2 for times of between 6 and 12 hours. SO_2 concentrations lay between 15 and 150 ppb; NO_2 concentrations were typically 300 ppb. 48 measurements of SO_2 uptake were performed and 4 of NO_2 uptake. Depth profiles of sulfur and nitrogen within the snow have yielded deposition velocities.

The surface deposition velocity of SO_2 to snowpack was found experimentally to average 0.06 cm s^{-1}; little effect was observed for changes in illumination, temperature and ozone concentrations. Surface deposition velocity of NO_2 averaged 0.005 cm s^{-1} in the dark and 0.012 in sunlight.

A theoretical model of SO_2 uptake by snow in the presence of O_3 and H_2O_2 has been developed. Agreement with experimentally observed profiles and deposition velocities is excellent. The model predicts a deposition velocity that decreases with time, with increasing SO_2 concentrations, with decreasing ozone concentrations and with decreasing liquid water content.

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Laboratory SO₂ deposition runs, using bubbler source: January 3 to February 13, 1986

Run	Time (Hr:Min)	SO₂ (ppbv) before/after	O₃ (ppb)	Temperature Range (°C)	Sun?	Melting?	Approx. age of snow	Snow ρ (g cm⁻³)	Liquid Water Content	Air Perm. †	Flux (10^{-12} g cm⁻² s⁻¹)	V (cm s⁻¹)	Comments
1-04-B	5:38	159.5	106	-1.5	no	at start	old	.42	---	210*	16.2	0.046	Snow sampling problems due to refreezing
1-05-A	6:46	27.2	0	-1	no	no	old	.38	---	210*	1.2	.021	Droplets on air input wall, snow not sampled deeply
1-05-B	12:18	27.2/33.6	34	-1	no	no	old	.37	---	210*	3.2	.048	Variable SO₂ input
1-06-A	11:18	33.6	0	-1(-1:+1)	no	no	old	.39	---	210*	7.2	.098	Snow recovery problems, snow not sampled below cut 5
1-07-A	9:06	20.3	0	0.5(+1:-0.5)	no	yes	old	.39	---	210*	3.9	.088	--
1-08-A	10:24	19.6	0	-6.0	no	no	old	.36	---	65	2.5	.058	Air intake wall icy
1-09-A	6:33	44.1/41.3	0	-1(-3:+1)	yes	yes!	old	.41	---	210*	13.7	.15	Considerable draining, interesting profile
1-09-B	10:31	41.3/32.4	0	+0.2	no	yes	old	.42	---	210*	1.5	.017	Variable SO₂, no draining
1-10-A	6:44	32.5	5+311	+1.8(-2.2:+3.8)	yes	yes	old	.40	---	210*	10.1	.14	Considerable draining, O₃ conc. wildly variable, O₃ often interrupts
1-11-A	6:19	12.5/29.1	67+122	-0.8(-3.5:0)	yes	yes	old	.39	---	210*	19.0	.41	Variable SO₂, considerable draining
1-12-A	6:15	122.5/46.1	0	+0.9(-4.1:+1.5)	yes	yes	old	.40	---	210*	41.5	.22	Variable SO₂, considerable draining, snow recovery prob (frozen block)
1-14-A	6:00	68.4/116.4	0	-7.2(-8.5:-3.6)	yes	no	old	.42	---	210*	7.2	.035	Variable SO₂, snow recovery probs (frozen block)
1-18-A	6:01	83.1/52.0	0	-3(-7.8:-1.6)	yes	yes!	old	.42	---	210*	9.1	.061	Variable SO₂, considerable draining
1-19-A	6:04	124.6/120.9	57+90	-4.8(-5.7:-3.8)	yes	yes	old	.40	---	210*	9.8	.036	Stable SO₂, snow recovery probs (frozen block)
1-20-A	6:08	101.2/71.8	62+84	-2(-4:-0.5)	yes	yes	old	.43	---	270*	10.6	.055	Variable SO₂, some draining
1-21-A	6:08	89.1/94.1	226+303	-8(-10.1:-6.6)	yes	yes	old	.40	---	270*	11.0	.055	Stable SO₂, snow recovery probs (frozen block)
1-22-A	6:08	185.5/94.1	230+289	-5.4(-7.5:-20)	yes	yes	old	---	---	210*	12.5	.041	Variable SO₂, snow recovery probs (frozen block)
1-23-A	6:03	114.1/93.2	297	-2.5(-3.4:-1.3)	yes	yes	old	.39	---	210*	14.7	.064	Somewhat variable SO₂, frozen block
1-24-A	6:07	152.8/142.0	71	-5.8(-8.4:-4.8	yes	a little	old	.40	---	210*	21.3	.066	Stable SO₂, good snow recovery with frozen block
2-02-A	6:00	30.0/17.9	0	-0.10	no	yes	old	.37	0.10	210	10.7	.20	Variable SO₂, some draining
2-03-A	6:00	30.1/26.7	0	-2.9(-3.2:+2.8)	no	yes	2 day	.18	---	288	14.1	.23	Heterogeneous snow composition complicates analysis,
2-04-A	6:02	27.5/27.0	0	-2.4	no	no	0 day	.11	---	380	4.5	.075	Stable SO₂, clumping, snow recovery probs (no snow lifter), flat SO₄= profile
2-05-A	6:09	22.5/27.4	0	-2.4	no	no	2 day	.16	---	1060	3.2	.058	SO₄= background in blanks and SO₂ variable
2-06-A	6:04	24.8/30.6	0	-2.1	no	no	0 day	.10	---	1621	4.1	.067	Heterogeneous snow, blanks by regression
2-08-A	6:06	43.2/30.8	0	-2.2	no	no	2 day	.16	---	171	3.1	.038	Variable SO₂, clumpy snow
2-09-A	6:00	15.2/23.8	0	-2.2	no	no	1 day	.07	---	274	2.5	.058	Variable SO₂, clumpy snow
2-10-A	6:07	31.0/20.3	0	-1.9	no	no	1 day	.08	---	540	2.2	.039	Air partially blocked with ice, variable SO₂ input
2-11-A	6:01	37.5/46.2	0	-2(-6.1:-2.6)	no	no	2 day	.14	---	244	2.8	.031	Stable SO₂, heterogeneous, blanks by regression
2-12-A	6:05	4.4/18.3	0	-4.3(-6.1:-2.6)	yes	a little	3 day	.24	---	677	3.0	.12	Variable SO₂, melting followed by freezing

Laboratory SO₂ deposition runs, using tank SO₂: February 14 to March 23, 1986

Run	Time (Hr:Min)	SO₂ (ppbv) before/after	O₃ (ppb)	Temperature Range (°C)	Sun?	Melting?	Approx. age of snow	Snow ρ (g cm⁻³)	Liquid Water Content	Air Perm. †	Flux (10^{-12} g cm⁻² s⁻¹)	V (cm s⁻¹)	Comments
2-14-A	6:10	95.6	0	-2.2(-3.7:-1.7)	no	at start	5 day	.37	---	---	6.5	.031	Variable blanks, unusual flat profile
2-16-A	6:01	98.9/84.5	0	-2.4	no	no	1 day	.33	---	---	8.6	.043	Air intake fogged up, clumpy snow
2-17-A	6:00	80.7/91.2	0	-0.2	no	yes	2 day	.27	0.18	2000	13.4	.071	Air intake fogged up, clumpy snow, no sign of draining
2-18-B	6:00	80.0	0	0	no	yes	3 day	.41	0.29	2200	11.2	.063	Draining occurred, end time not immediately recorded
2-21-A	5:50	79.6/75.6	0	-3.4(-3.8:-1.8)	no	at start	6 day	.39	---	170*	4.2	.025	Air intake droplets and frost, frozen block
2-24-A	5:58	70.9/70.0	0	-0.1	no	yes	9 day	.38	0.16	170*	14.5	.093	Bottom used as blank, no draining
2-25-A	6:02	75.3/83.0	0	-0.1	no	yes	10 day	.40	0.12	170*	10.1	.059	Attempt to duplicate 2-24-A, little draining
2-26-A	6:22	79.7/81.2	0	-2.3	no	no	11 day	.40	---	170*	5.0	.028	Bottom used as blank (nonrepresentative blanks)
3-02-A	12:01	83.7	0	-2.3	no	no	old	.41	---	210*	2.8	.015	12-hr. run for Deena's melt experiments
3-03-A	11:00	83.7/78.8	0	-2.3	no	no	old	.44	---	270*	2.0	.012	11-hr run
3-05-A	10:03	81.8/83.7	0	+0.2	no	yes	old	.40	0.13	210*	7.9	.043	A little draining
3-05-B	11:19	83.8/83.2	0	+0.2	no	yes	old	.42	---	210*	4.9	.027	Some draining
3-07-A	6:00	74.0/86.4	0	+0.2	no	yes	---	.42	---	210*	11.2	.063	Erratic IC baseline
3-09-A	6:02	77.1+35(?)	142	-2.0	no	no	1 day	.21	---	90*	4.2	.025	SO₂ conc. fell throughout run, clumpy new snow
3-12-A	6:00	83.0/84.2	142	-2.0	no	no	2 day	.20	---	80*	8.6	.046	Clumpy snow
3-12-B	12:07	84.2/78.7	0	-2.0	no	no	old	---	---	210*	3.5	.020	Snow orig. for melt run, then prep. for gas run
3-13-A	6:15	76.9/80.1	168	-9(-13.3:-5.6)	yes	no	2 day	.18	---	320*	9.3	.054	Bottom used as blank (unrepresentative blanks), no teflon tape on rods, clumping
3-20-A	6:16	81.9/76.1	82	-9.5(-13.3:-5.6)	yes	along rods	4 day	.20	---	160*	8.6	.049	--
3-21-A	6:09	68.0/75.4	0	-8(-12.1:-2.4)	yes	yes	5 day	.25	0.14	70*	15.0	.095	Considerable draining

* Estimate based on similar snow type and density.   † Units are cm² s⁻¹ [cm of H₂O]⁻¹
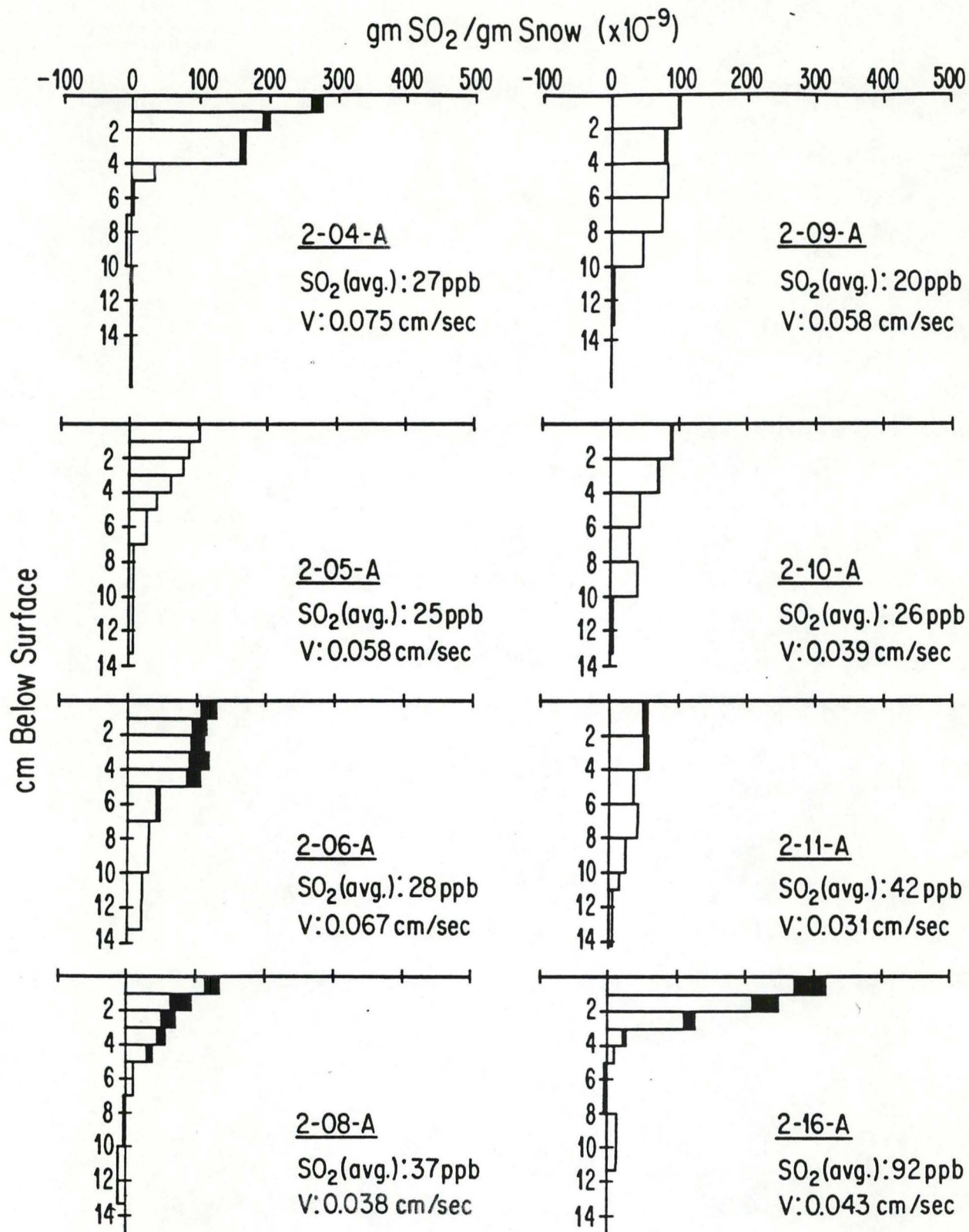
Figure A-1   Profiles for low-density, new snow, at temperatures from −1.9°C to −2.4°C, and with no sunlight or ozone.
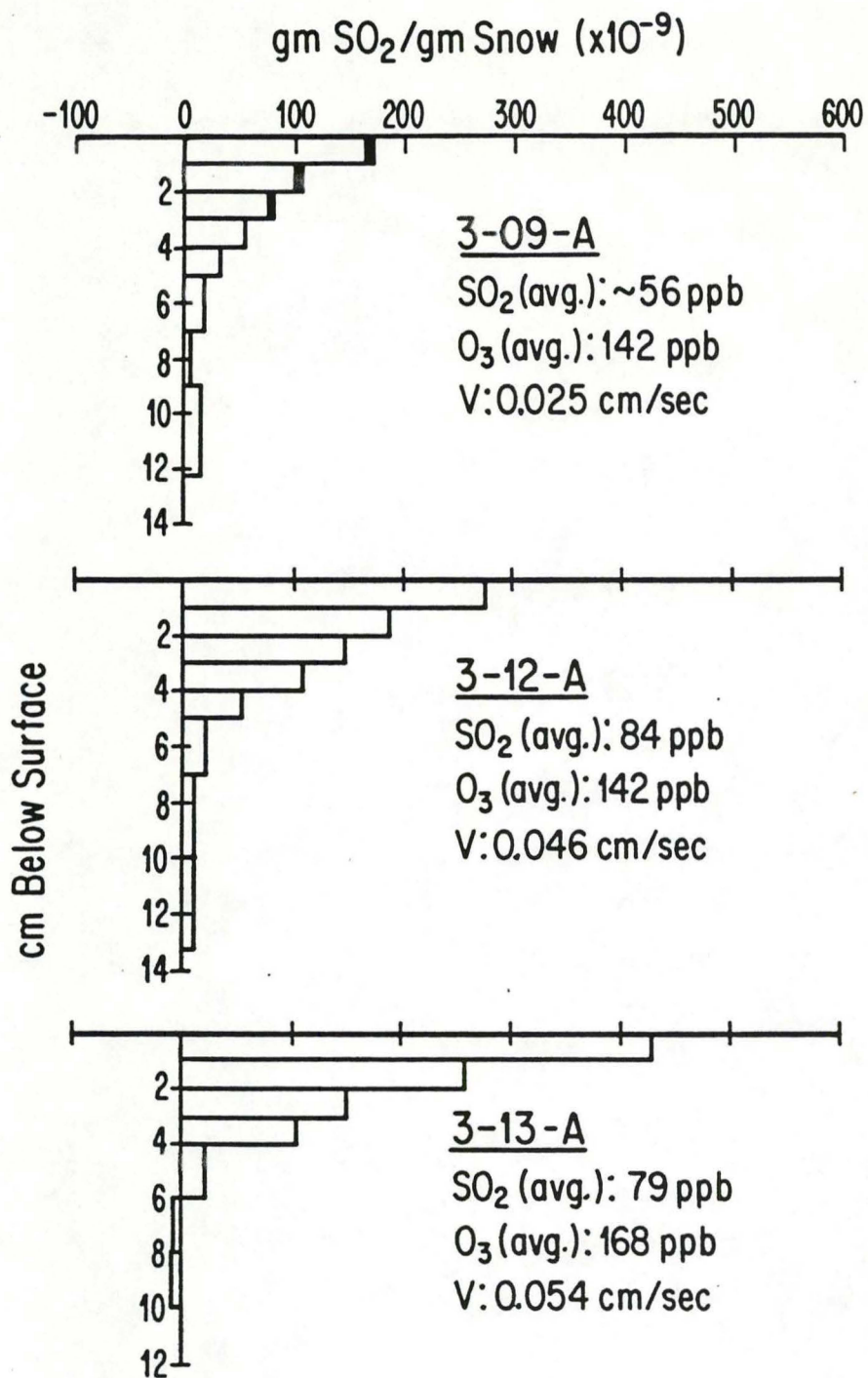
Figure A-2   Profiles for medium-density, new snow at -2°C, with no sunlight, but with 140 ppbv ozone.

gm SO$_2$/gm Snow (x10^{-9})

2-21-A
SO$_2$ (avg.): 78 ppb
V: 0.025 cm/sec

3-03-A
SO$_2$ (avg.): 81 ppb
V: 0.012 cm/sec

2-26-A
SO$_2$ (avg.): 80 ppb
V: 0.028 cm/sec

3-12-B
SO$_2$ (avg.): 81 ppb
V: 0.020 cm/sec

3-02-A
SO$_2$: 83.7 ppb
V: 0.015 cm/sec

cm Below Surface
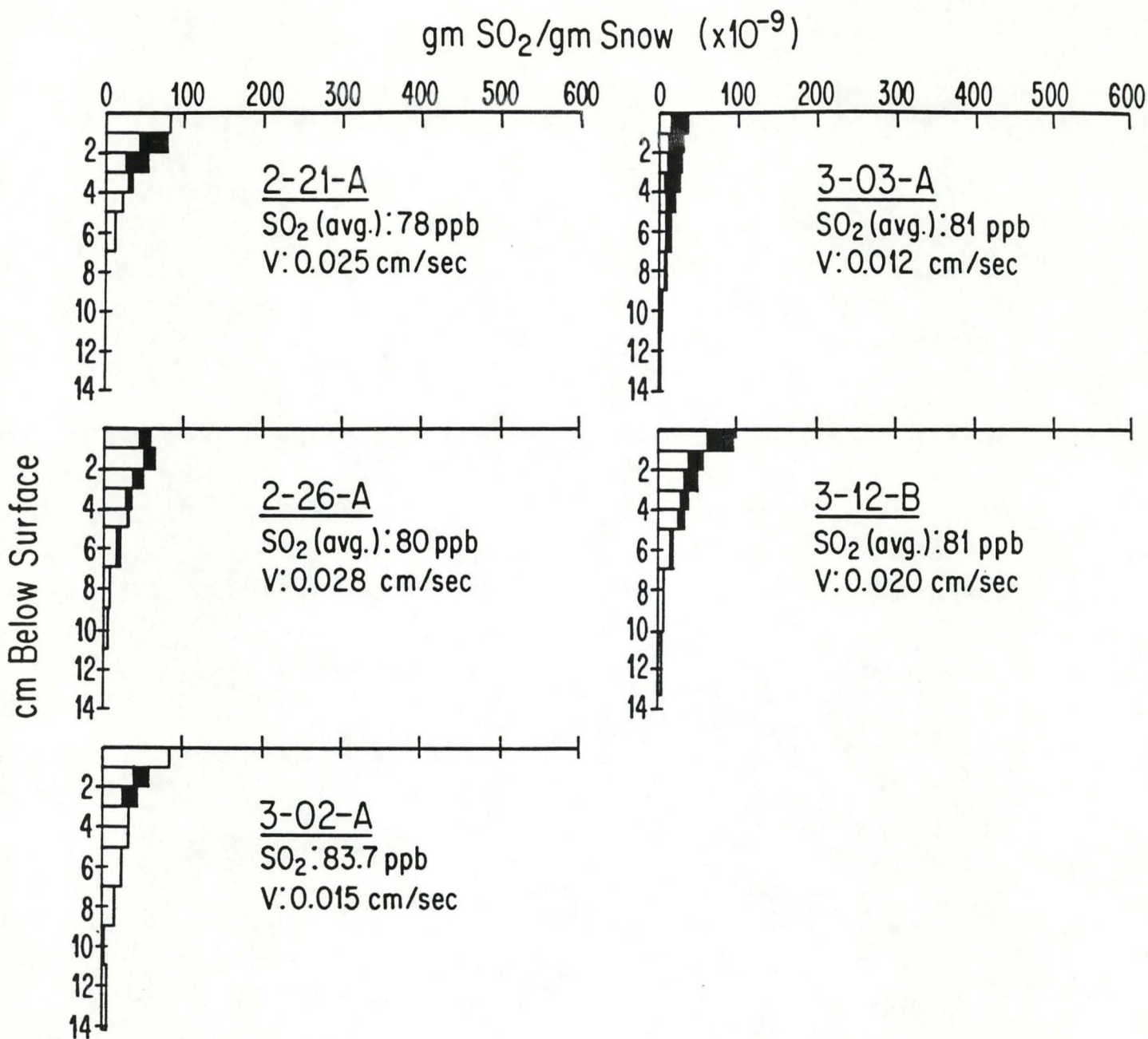
Figure   A-3   Profiles for older snow at -2.0 to -2.3°C, with no sunlight or
ozone.

gm SO$_2$/gm Snow (x10^{-9})

1-04-B

SO$_2$: 160 ppb
O$_3$ (avg.): 106 ppb
V: 0.046 cm/sec

1-05-A

SO$_2$: 27 ppb
O$_3$ (avg.): 0 ppb
V: 0.021 cm/sec

1-05-B

SO$_2$ (avg.): 30 ppb
O$_3$ (avg.): 34 ppb
V: 0.048 cm/sec

1-06-A

SO$_2$: 34 ppb
O$_3$: 0 ppb
V: 0.098 cm/sec

1-08-A

SO$_2$: 20 ppb
O$_3$: 0 ppb
V: 0.058 cm/sec

cm Below Surface
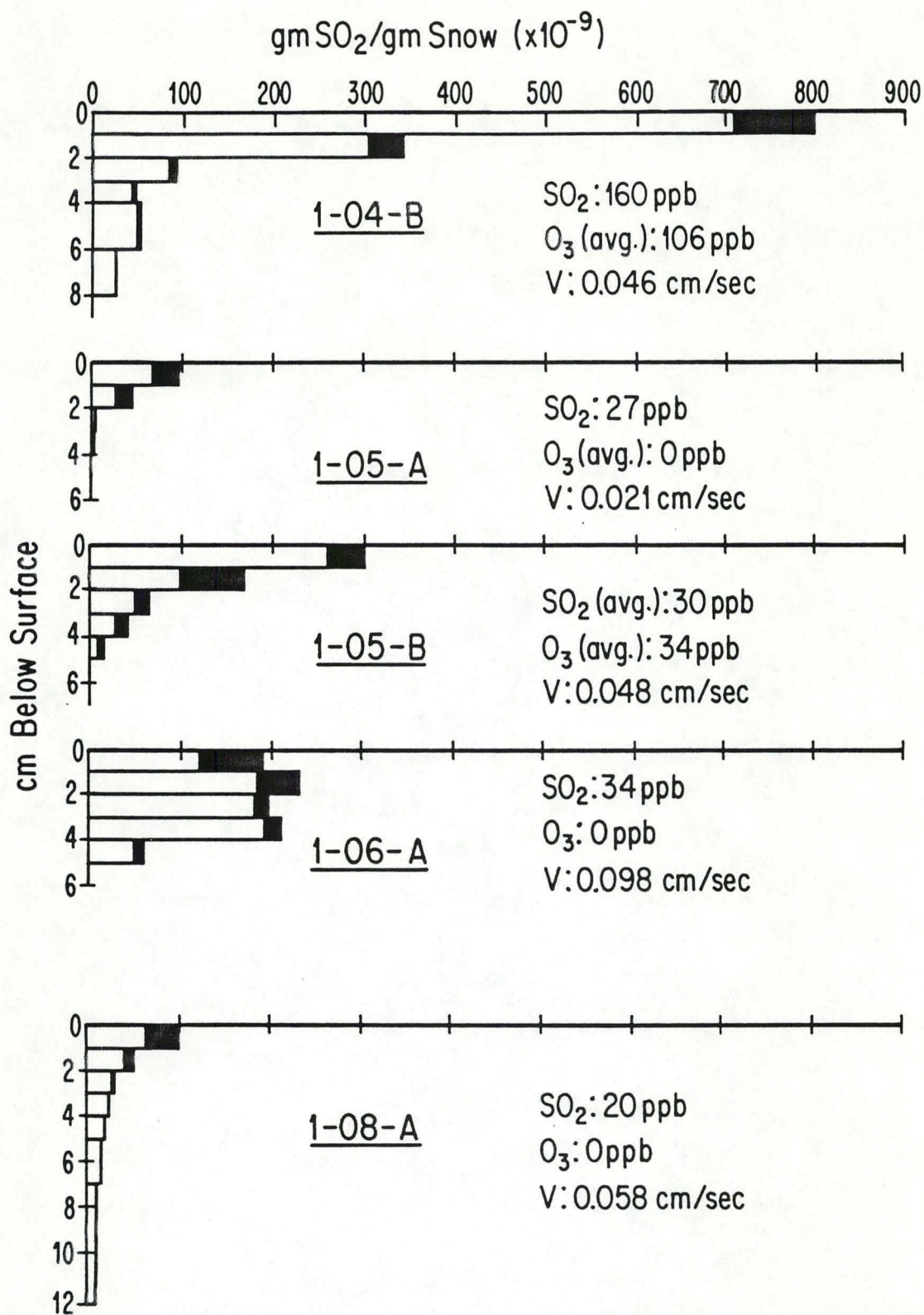
Figure A-4   Profiles for other low-temperature experiments on older snow.

gm SO$_2$/gm Snow (x10^{-9})

1-07-A
SO$_2$: 20 ppb
V: 0.088 cm/sec

2-25-A
SO$_2$ (avg.): 79 ppb
V: 0.059 cm/sec

1-09-B
SO$_2$ (avg.): 37 ppb
V: 0.017 cm/sec

3-05-A
SO$_2$ (avg.): 83 ppb
V: 0.043 cm/sec

cm Below Surface

2-02-A
SO$_2$ (avg.): 24 ppb
V: 0.20 cm/sec

3-05-B
SO$_2$ (avg.): 84 ppb
V: 0.027 cm/sec

2-18-B
SO$_2$ (avg.): 80 ppb
V: 0.063 cm/sec

3-07-A
SO$_2$ (avg.): 80 ppb
V: 0.063 cm/sec

2-24-A
SO$_2$ (avg.): 70 ppb
V: 0.093 cm/sec

Figure A-5   Profiles for older snow near 0°C, with little or no draining, and
with no sunlight.

Figure A-6   Profiles for medium-density, new snow near 0°C, with no draining, and with no sunlight or ozone.

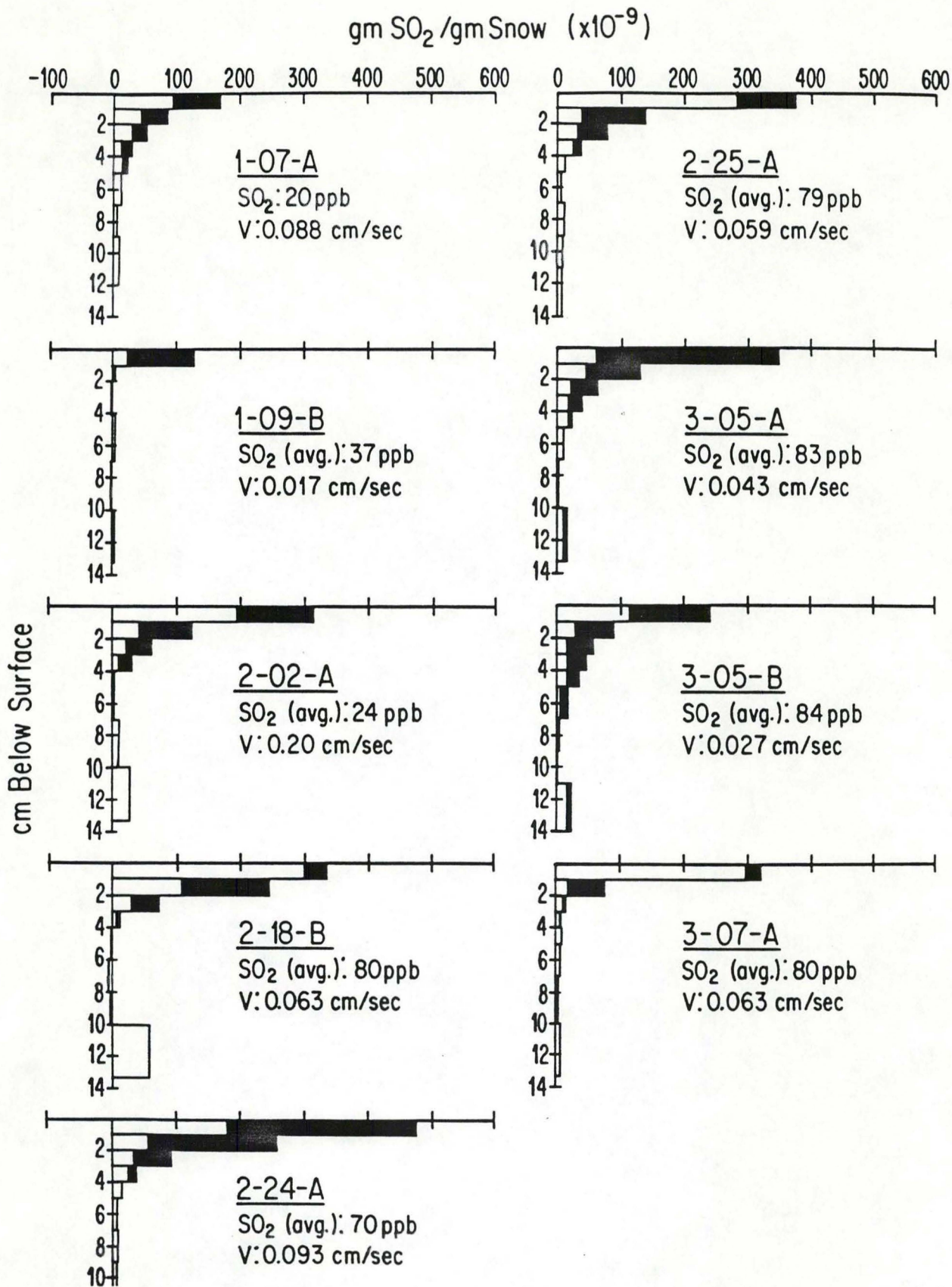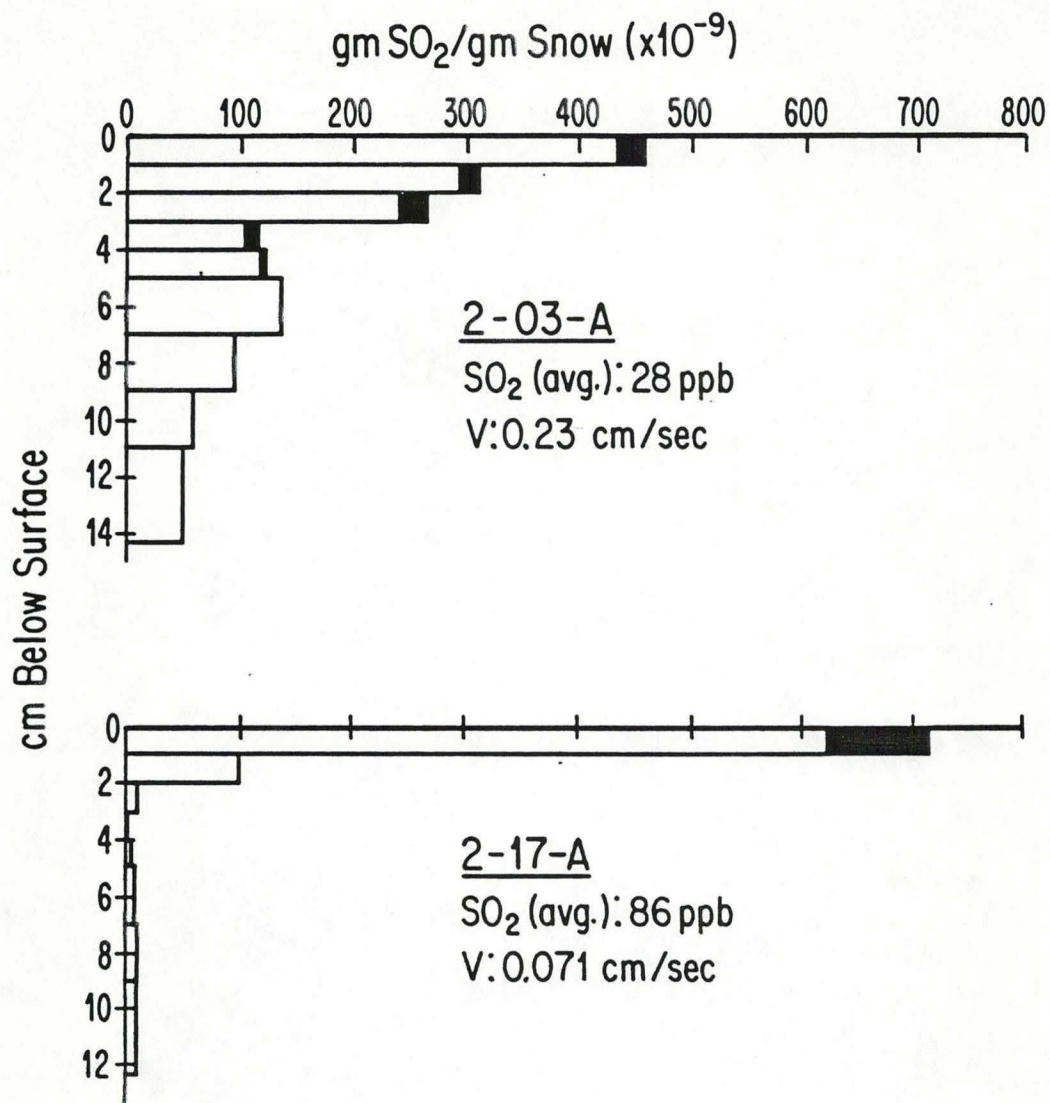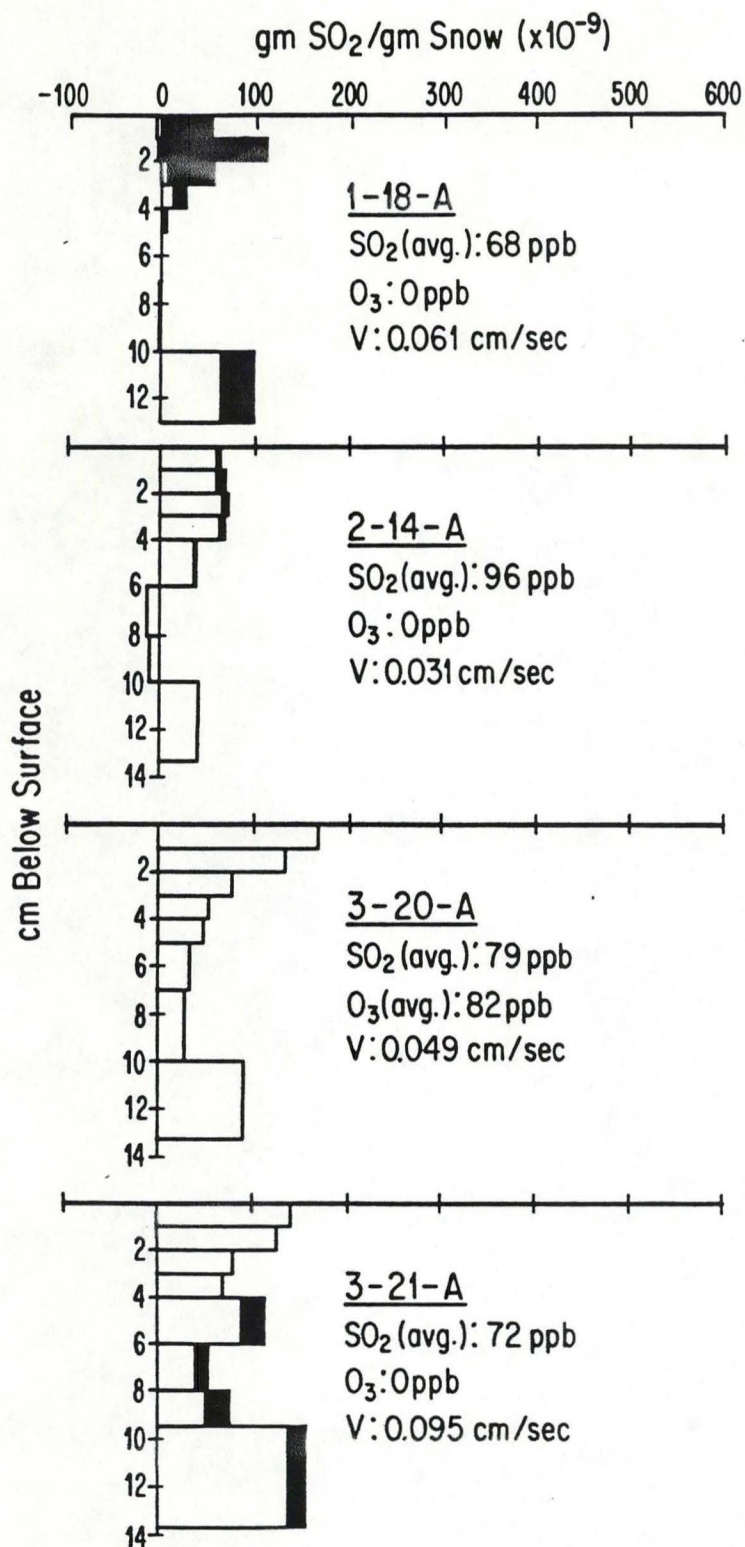gm SO$_2$/gm Snow (x10^{-9})

1-14-A
SO$_2$ (avg.): 92 ppb
O$_3$: 0 ppb
V: 0.035 cm/sec
no melting

1-22-A
SO$_2$ (avg.): 140 ppb
O$_3$ (avg.): 260 ppb
V: 0.041 cm/sec
with melting

1-19-A
SO$_2$ (avg.): 123 ppb
O$_3$ (avg.): 74 ppb
V: 0.036 cm/sec
with melting

1-23-A
SO$_2$ (avg.): 104 ppb
O$_3$ (avg.): 297 ppb
V: 0.064 cm/sec
with melting

1-20-A
SO$_2$ (avg.): 87 ppb
O$_3$ (avg.): 73 ppb
V: 0.055 cm/sec
with melting

1-24-A
SO$_2$ (avg.): 147 ppb
O$_3$ (avg.): 71 ppb
V: 0.066 cm/sec
little melting

1-21-A
SO$_2$ (avg.): 92 ppb
O$_3$: 265 ppb
V: 0.055 cm/sec
no melting

2-12-A
SO$_2$ (avg.): 11 ppb
O$_3$: 0 ppb
V: 0.12 cm/sec
little melting

cm Below Surface

Figure A-7   Profiles for older snow, with surface melting but without signifi-
cant draining, with sunlight.

Figure A-8 Profiles for medium—density new snow, with significant draining due to surface melting by sunlight.

gm SO₂/gm Snow (x10⁻⁹)

1-09-A
SO₂ (avg.): 43 ppb
O₃: 0 ppb
V: 0.15 cm/sec

1-10-A
SO₂: 33 ppb
O₃ (avg.): 158 ppb
V: 0.14 cm/sec

1-11-A
SO₂ (avg.): 21 ppb
O₃ (avg.): 95 ppb
V: 0.41 cm/sec

1-12-A
SO₂ (avg.): 84 ppb
O₃: 0 ppb
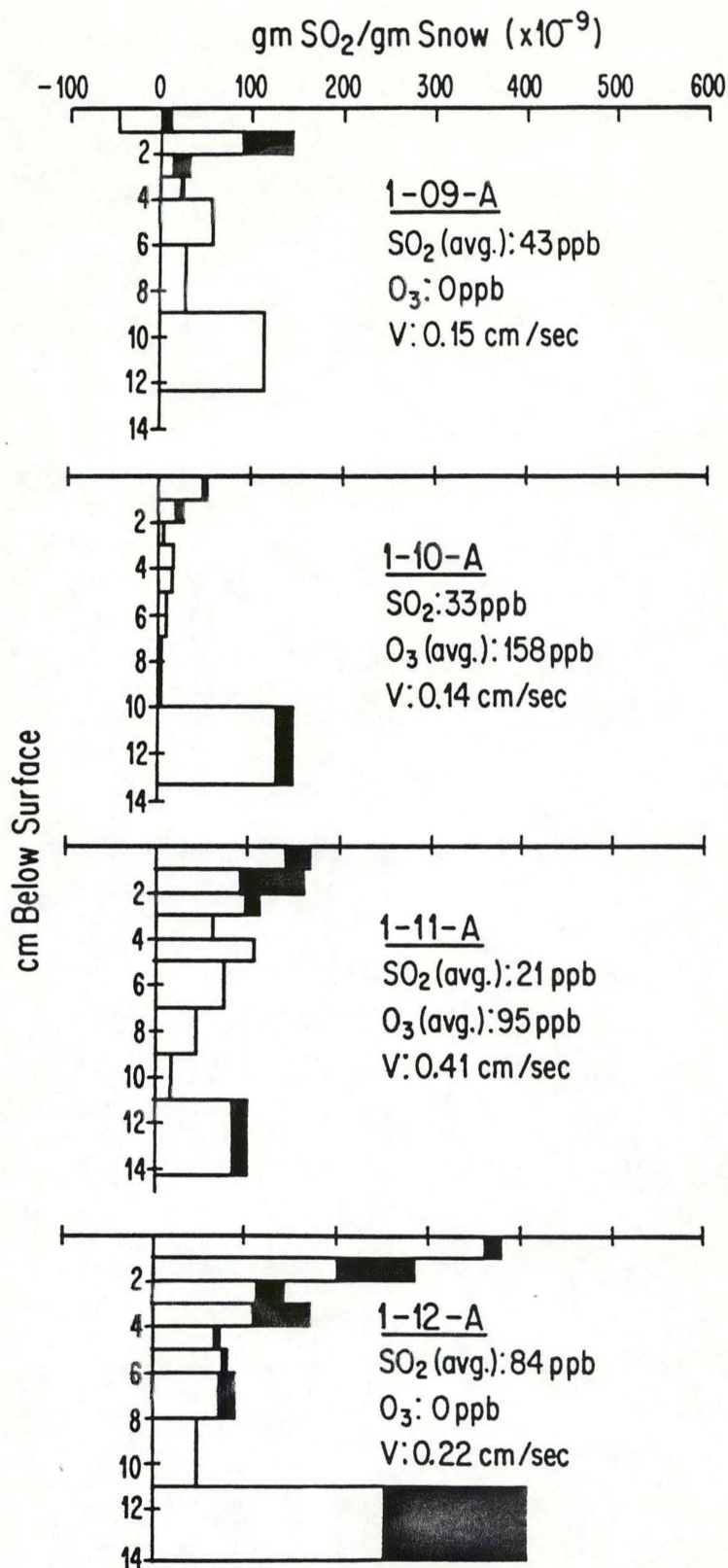V: 0.22 cm/sec

cm Below Surface

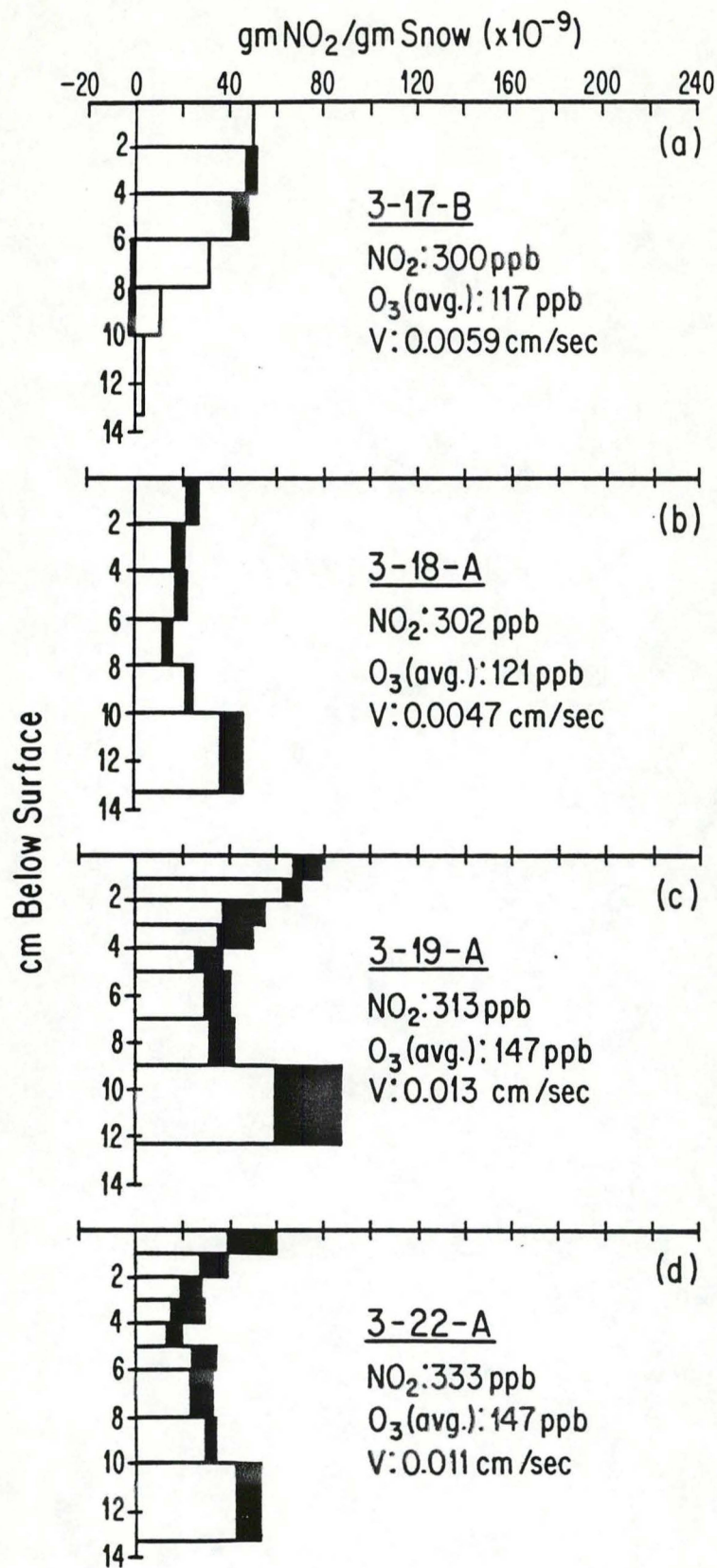**Figure A-9**   Profiles for older snow, with significant draining due to surface melting by sunlight.

Figure A-10   Profiles for NO_2 deposition